New Supported [Ru_6N] Clusters as a Potential Transition Metal Nitride Catalyst

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Nitrido-ruthenium cluster [Ru_6N] catalysts were prepared by reacting [$Ru_6N(CO)_{16}$]$^-$ cluster with MgO, K^+-doped MgO or Cs^+-doped MgO as a potential ruthenium nitride catalyst. The [Ru_6N] unit remained in reaction conditions, and exhibited higher activities in ammonia synthesis than conventional Ru catalysts or Ru clusters prepared from [$Ru_6C(CO)_{16}Me$]$^-$ or [$Ru_6(CO)_{18}$]$^{2-}$.

Metal clusters are expected to be effective catalysts associated with multiple metal sites. Specific activities to oxygenated compounds (MeOH, H_2CO, Me_2O) from CO + H_2 were reported on carbido-Ru clusters [Ru_6C] supported on MgO, La_2O_3, or TiO_2.[1-3] Reversible expansion/shrink of [Ru_6C] framework observed by EXAFS in the CO-H_2 reaction conditions facilitated the access to Ru sites and dissociation of H_2 by elongating the Ru-Ru distance.[1,2,4] In this paper, we report the formation of new nitrido-Ru clusters [Ru_6N] on oxides and catalysis promoted by nitrido nitrogen.

[$N(PPh_3)_2$]$^+$[$Ru_6N(CO)_{16}$]$^-$ 1 [5] was supported on MgO, K^+/MgO, Cs^+/MgO, or Al_2O_3 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 m^2g^{-1}) was prepared from $Mg(OH)_2$ (99.99%) by heating at 773 K (2h) in vacuum. Water solution of Cs_2CO_3 or K_2CO_3 was impregnated on MgO, followed by treatments in O_2/H_2 at 773 K. The Al_2O_3 (aerosil C) (100 m^2g^{-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 Al_2O_3. The supported nitrido-Ru clusters are denoted as [Ru_6N]/oxide. [$N(PPh_3)_2$]$^+$ [$Ru_6C(CO)_{16}Me$]$^-$ or [$N(PPh_3)_2$]$^+_2$[$Ru_6(CO)_{18}$]$^{2-}$ 2 was supported on MgO in a similar manner to the case of 1. These supported Ru clusters are denoted as [Ru_6C]/MgO and [Ru_6]/MgO, respectively. The conventional Ru/MgO, Ru-Cs^+/MgO, and Ru/Al_2O_3 catalysts were prepared from $Ru(NO)(NO_3)_3$ (Ru 2.5 wt%).

The N_2-H_2 reactions were carried out under 101 kPa of reaction gas (P_{N_2}/P_{H_2} = 1/3) at 588 K in a flow system (flow rate 60 cm^3 min^{-1}). The H_2-D_2 exchange reactions were carried out under 6.7 kPa of H_2 and 6.7 kPa of D_2 at 273 K in a closed circulating system (100 cm^3). As pretreatment, incipient supported clusters were heated in vacuum at 813 K except for [Ru_6N]-Cs^+/MgO and [Ru_6N]-K^+/MgO (673 K), followed by treatment in H_2 (T_{H_2} = 588 - 773 K). The temperature in H_2 was specified at the end of denotation such as [Ru_6N]/MgO-588H for sample treated in H_2 at 588 K. Produced ammonia was analyzed by the decrease of electron conductivity of 0.004 - 0.002 N-H_2SO_4 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 H_2-adsorption measurements for conventional catalysts. The TOF of H_2-D_2 exchange reactions on supported clusters and conventional Ru catalysts are shown in Table 1. The order was [Ru_6N]/MgO-588H (2600) > [Ru_6C]/MgO-588H (2400) > [Ru_6N]-Cs^+/MgO-588H (1900) > [Ru_6C]/MgO-773H (700) ~ [Ru_6]/MgO-588H (700) >> [Ru_6N]/Al_2O_3-588H (34) >> conv. Ru/MgO (1.3). The supported [Ru_6N] clusters treated in H_2 at 588 K were comparable to supported [Ru_6C], and superior to supported [Ru_6] or conventional Ru catalysts for hydrogen activation.

As an example of hydrogenations, the N_2-H_2 reactions (588 K) were examined related to this hydrogen activation (Table 1). The TOF of supported nitrido-Ru cluster on MgO when treated in H_2 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 [Ru_6N]/Al_2O_3 exhibited no activities after the H_2-treatment at 588 - 773 K though conventional Ru/Al_2O_3 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 [$Ru_6N(CO)_{16}$]$^-$ (0.28 - 1.8) > [$Ru_6C(CO)_{16}Me$]$^-$ (0.27 - 1.2) > [$Ru_6(CO)_{18}$]$^{2-}$ (0.22) > Ru salt (0.20) (Table 1). The [Ru_6N]/MgO was superior to [Ru_6C]/MgO by 1.5 times, and superior to the others in the order in the comparison for the samples in H_2 at 588 K. It should be noted that the activities on [Ru_6N]/MgO and [Ru_6C]/MgO had strong dependence on T_{H_2}. The TOF for [Ru_6N]/MgO-773H (0.28) was only 15% of that for [Ru_6N]/MgO-588H (1.8), whereas the dependence on T_{H_2} was not observed for [Ru_6]/MgO treated in H_2 at 588 - 773 K. We studied temperature programmed reduction (TPR) in H_2 by mass spectroscopy for incipient [Ru_6N]/MgO, [Ru_6N]-Cs^+/MgO, and [Ru_6]/MgO. These spectra had common peaks of NH_3 around 510 K, but higher temperature-peaks of NH_3 was observed around 660 K only for [Ru_6N]/MgO and [Ru_6N]-Cs^+/MgO. As the former desorption temperature (around 510 K) coincided with the decomposition temperature of the IR peak of [$N(PPh_3)_2$]$^+$ (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 H_2 for [Ru_6C]/MgO (carbido C desorbed as CH_4) had a peak around 560 K,[1] suggesting that this cluster transformation was the cause of the TOF decrease from 1.2 (T_{H_2} = 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 [Ru_6N]/MgO, [Ru_6N]-K^+/MgO, and [Ru_6N]-Cs^+/MgO after heating in vacuum (813 or 673 K) and in H_2 (588 K), similar to the value for cluster 1 (= 4), indicating that the [Ru_6N] unit remained on MgO, K^+/MgO, and Cs^+/MgO compared to the Ru trimers such as MgO-supported $Ru_3(CO)_{12}$ (in H_2 at 723 K) (N_{Ru-Ru} = 1.7)[2] and [Ru_6N]/Al_2O_3-588H (2.0) or aggregated clusters such as [Ru_6N]/MgO-773H (6.6) and [Ru_6]/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 [Ru_6C]/MgO lost carbido C and was transformed to [Ru_6] on MgO in H_2 at 623 - 773 K.[1] Hence, the TOF ratio of [Ru_6N] : [Ru_6C] : [Ru_6] species on MgO was 100 : 67 : 14 from Table 1. Both [Ru_6N] and [Ru_6C] were very good for the H_2 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 $[Ru_6N(CO)_{16}]^-$, $[Ru_6C(CO)_{16}Me]^-$, or $[Ru_6(CO)_{18}]^{2-}$ Clusters, and Conventional Ru Catalysts

T_{reac}/K		588	273
P_{N_2}/kPa		25.3	
P_{H_2}/kPa		76.0	6.7
P_{D_2}/kPa			6.7
sample	T_{H_2}/K		
$[Ru_6N(CO)_{16}]^-$/MgO	588	1.8	2600
	773	0.28	970
$[Ru_6N(CO)_{16}]^-$-K^+/MgO	588	3.2	
$[Ru_6N(CO)_{16}]^-$-Cs^+/MgO	588	6.6	1900
$[Ru_6C(CO)_{16}Me]^-$/MgO	588	1.2	2400
	773	0.27	700
$[Ru_6(CO)_{18}]^{2-}$/MgO	588	0.22	700
conv. Ru/MgO	773	0.20	1.3
conv. Ru-Cs^+/MgO	773	1.7	
$[Ru_6N(CO)_{16}]^-$/Al_2O_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 $[Ru_6X]$ (X = N, 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 donor[9] were also important, probably to the N_2 dissociation process. The detailed discussion on promoted ammonia synthesis on $[Ru_6N]$ clusters accompanied with cluster expansion/shrink ($r_{Ru\text{-}Ru} = 0.263 \rightleftarrows 0.271$ 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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