Supplementary Information

Combined KH/Alkaline-Earth Amides Catalysts for

Hydrogenation of Alkenes

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1. General Information

All manipulations of air- and moisture-sensitive compounds were performed under an argon atmosphere by use of standard Schlenk techniques or under a nitrogen atmosphere in a Mikrouna glovebox. Benzene-*d*₆ and substituted alkenes purchased from J&K, Alfa Aesar, Adamas and TCI were dried over CaH₂, degassed and kept in a glovebox prior to use. KH (30% w/w in mineral oil) purchased from Alfa Aesar was washed thoroughly with hexane and kept in a glovebox. LiHMDS (1.0 M in THF) and NaHMDS (1.0 M in THF) and KHMDS (1.0 M in THF) (1.0 M in THF) was purchased from J&K. After a process for removing the solvents under vacuum, the metal amides were kept as solids under -30 °C in a glovebox. High purity nitrogen (99.999%) and hydrogen (99.999%) gas were purchased from Tianjin Huanyu Gas Co., Ltd. Ca(HMDS)₂·(THF)₂^[1], Ca(HMDS)₂·Et₂O^[2] and Zn(HMDS)₂^[3] were synthesized according to literatures. ¹H NMR, ¹³C NMR were recorded on a Bruker AV 400 (400 MHz for ¹H, 101 MHz for ¹³C) instrument in C₆D₆. The inductively coupled plasma optical emission spectrometer (ICP-OES) was performed by SPECTRO-BLUE.

2. Additional Condition Optimization

Catalytic hydrogenation of *trans*-β-methylstyrene

We also evaluated catalytic hydrogenation of *trans*- β -methylstyrene (**1c**) by various catalysts at 80 °C for 48 h. The combinations of KH with calcium and magnesium amide were proved to be efficient catalysts for this reaction (Table S1, entries 1-2). KH could not realize this reaction in C₆D₆ or THF, and these metal amides themselves were also sluggish for the hydrogenation reaction (Table S1, entries 3-6). When carried out in THF solvent, **1c** could not be hydrogenated (Table S1, entry 7). The hydrogenation reaction was not efficient when using the mixture of alkali metal and zinc amides with KH (Table S1, entries 8-11).

	Ph ^{Me} + 1c	H ₂ <u>Catalyst (10 mol %</u> 6 bar) C ₆ D ₆ , 80 °C, 48 h	b) → H Ph → Me 2c H
Entry	Catalyst		Yield (%) ^[b]
1	KH + Ca	$(\text{HMDS})_2 \cdot (\text{THF})_2$	99
2	KH + Mg	$g(HMDS)_2 \cdot Et_2O$	99
3	KH		<5
4 ^[c]	KH		<5
5	Ca(HMD	$(S)_2 \cdot (THF)_2$	24
6	Mg(HMI	$DS)_2 \cdot Et_2O$	<5
7 ^[c]	KH + Ca	$(\text{HMDS})_2 \cdot (\text{THF})_2$	<5
8	KH + LiI	HMDS·THF	12
9	KH + Na	HMDS·(THF)0.9	11
10	KH + KH	IMDS · (THF)0.8	24
11	KH + Zn	(HMDS) ₂	10

Table S1. Hydrogenation of *trans*-β-methylstyrene.^[a]

[a] Conditions: *trans*- β -methylstyrene (1c) (0.3 mmol), H₂ (6 bar), KH (10 mol %), metal amides (10 mol %), C₆D₆ (0.5 mL), 80 °C, 48 h; [b] NMR yields with hexamethylbenzene as an internal standard; [c] THF as solvent.

3. Typical Procedure for Hydrogenation Reaction

Typical procedure for hydrogenation reaction of 1,1-diphenylethylene

In a glovebox, to an oven-dried steel autoclave (25 mL) were added KH (0.03 mmol, 1.2 mg), $Ca(HMDS)_2 (THF)_2 (0.03 mmol, 15.2 mg)$, hexamethylbenzene (internal standard, about 15 mg) and $C_6D_6 (0.5 mL)$. The mixture was stirred at ambient temperature for 5 minutes, then was added 1,1-diphenylethylene (**1a**, 0.30 mmol, 54 mg). The autoclave was sealed, pressurized with 6 bar of H₂ and stirred at 60 °C for 5 hours. The yield of 99% were obtained from the relative ¹H NMR integrations of the internal standard and product.

Typical procedure for hydrogenation reaction of 1-octene

In a glovebox, to an oven-dried steel autoclave (25 mL) were added KH (0.03 mmol, 1.2 mg), $Ca(HMDS)_2 \cdot (THF)_2$ (0.03 mmol, 15.2 mg), and C_6D_6 (0.5 mL). The suspension was stirred at ambient temperature for 5 minutes, then 1-octene (1b, 0.3 mmol, 33.6 mg) was added. The autoclave was sealed, pressurized with 6 bar of H₂ and stirred at 100 °C for 24 hours. The yield of octane (75%) and 2-octene (23%) were determined by GC analysis with dodecane as an internal standard.

4. Mechanism Studies

4.1. The reaction between KH and $M(HMDS)_2 \cdot S_n$ (M = Ca and Mg).

In a glovebox, to a 25-mL shlenk tube were added KH (0.1 mmol, 4 mg), $M(HMDS)_2$. S_n (0.1 mmol, M = Ca, 50.5 mg or M = Mg, 41.9 mg) and solvent (THF or benzene, 0.5 mL). The tube was tightly sealed, removed from the glovebox and heated at 80 °C for 48 h. The suspension was then settled and filtrated through a 25 mm-Luer syringe filter to give a light yellow solution. The volatiles were removed under vacuum to provide a light yellow solid, which was then analyzed with ¹H NMR and ICP-OES.



Figure S1. ¹H NMR spectrum (C_6D_6) of the reaction of KH and $Ca(HMDS)_2 \cdot (THF)_2$ in benzene.

Table S2. ICP-OES analysis of the reaction between KH and $M(HMDS)_2 \cdot S_1$

entry	reactants	solvent	K (wt%)	Ca (wt%)
1	$\mathbf{K}\mathbf{H} + \mathbf{C}\mathbf{a}(\mathbf{H}\mathbf{M}\mathbf{D}\mathbf{S})_2 \cdot (\mathbf{T}\mathbf{H}\mathbf{F})_2$	benzene	17.5	17.5
2	$\mathbf{K}\mathbf{H} + \mathbf{C}\mathbf{a}(\mathbf{H}\mathbf{M}\mathbf{D}\mathbf{S})_2 \cdot (\mathbf{T}\mathbf{H}\mathbf{F})_2$	THF	18.6	17.7
3	K H + 3 Ca (HMDS) ₂ ·(THF) ₂	benzene	6.9	28.0
			K (wt%)	Mg (wt%)
4	$\mathbf{K}\mathbf{H} + \mathbf{M}\mathbf{g}(\mathbf{H}\mathbf{M}\mathbf{D}\mathbf{S})_2 \cdot \mathbf{E}\mathbf{t}_2\mathbf{O}$	benzene	14.8	12.9
5	\mathbf{K} H + $\mathbf{M}\mathbf{g}$ (HMDS) ₂ ·Et ₂ O	THF	16.1	15.5





Figure S3. $[KMg(HMDS)_2H]_2$ catalyzed hydrogenation of 1-octene (1b : 2b : 1b' = 6 : 86 : 8).

5. NMR Spectrum of Hydrogenation Reactions



Figure S5. $[KH + Ca(HMDS)_2 \cdot (THF)_2]$ catalyzed hydrogenation of 1,1-diphenylethene (hexamethylbenzene, 15.7 mg, 99% yield).^[5-8]



Figure S6. $[KH + Mg(HMDS)_2 \cdot Et_2O]$ catalyzed hydrogenation of 1,1-diphenylethene (hexamethylbenzene, 16.3 mg, 99% yield).



Figure S7. **[KH + Zn(HMDS)**₂] catalyzed hydrogenation of 1,1-diphenylethene (hexamethylbenzene, 16.0 mg, 99% yield).



Figure S8. [KH + KHMDS·(THF)_{0.8}] catalyzed hydrogenation of 1,1-diphenylethene (hexamethylbenzene, 11.3 mg, 99% yield).





Figure S9. ¹H NMR (400 MHz, C₆D₆) spectrum of 1-octene.



Figure S10. **[KH + Ca(HMDS)**₂·**(THF)**₂**]** catalyzed hydrogenation of 1-octene (98% conv.; 75% of n-octane and 23% of isomers).^[5]



Figure S11. **[KH + Mg(HMDS)**₂·**Et**₂**O]** catalyzed hydrogenation of 1-octene (96% conv.; 80% of n-octane and 16% of isomers).



Figure S13. [KH + Ca(HMDS)₂·(THF)₂] catalyzed hydrogenation of *trans*- β -methylstyrene (hexamethylbenzene, 16.5 mg, 99% yield).^[5]



Figure S14. **[KH + Mg(HMDS)**₂·**Et**₂**O]** catalyzed hydrogenation of *trans*- β -methylstyrene (hexamethylbenzene, 16.0 mg, 99% yield).



Figure S15. ¹H NMR (400 MHz, C₆D₆) spectrum of α-methylstyrene.



Figure S16. [KH + Mg(HMDS)₂·Et₂O] catalyzed hydrogenation of α -methylstyrene (97% yield).^[5-8]



Figure S17. [KH + Ca(HMDS)₂·(THF)₂] catalyzed hydrogenation of α -methylstyrene (99% yield).

3.32



Figure S18. ¹H NMR (400 MHz, C₆D₆) spectrum of 1,3-diphenylpropene.^[9]



Figure S19. [KH + Mg(HMDS)₂·Et₂O] catalyzed hydrogenation of 1,3-diphenylpropene (99% yield).



Figure S20. **[KH + Ca(HMDS)**₂·(**THF**)₂**]** catalyzed hydrogenation of 1,3-diphenylpropene (99% yield).



Figure S21. ¹H NMR (400 MHz, C₆D₆) spectrum of 1,2-diphenylethene.



Figure S22. [KH + Mg(HMDS)₂·Et₂O] catalyzed hydrogenation of 1,2-diphenylethene (97% yield).^[5-8]



Figure S23. **[KH + Ca(HMDS)**₂·(**THF**)₂**]** catalyzed hydrogenation of 1,2-diphenylethene (88% yield).







Figure S25. [KH + Mg(HMDS)₂·Et₂O] catalyzed hydrogenation of diphenylacetylene (88% yield).^[5-8]



Figure S26. [KH + Ca(HMDS)₂·(THF)₂] catalyzed hydrogenation of diphenylacetylene (96% yield).



Figure S27. ¹H NMR (400 MHz, C₆D₆) spectrum of styrene.



Figure S28. [KH + Mg(HMDS)₂·Et₂O] catalyzed hydrogenation of styrene using hexamethylbenzene (15.8 mg) as an internal standard (13.3 mg, 5% yield of ethylbenzene; 98% conv. for styrene; oligomers were detected by GC-MS: m/z: 210.1, 314.2, 405.0).^[8]



Figure S29. $[KH + Ca(HMDS)_2 \cdot (THF)_2]$ catalyzed hydrogenation of styrene using hexamethylbenzene (15.8 mg) as an internal standard (15.8 mg, 14% yield of ethylbenzene; 97% conv. for styrene; oligomers were detected by GC-MS: m/z: 210.1, 314.2, 405.0).









Figure S33. ¹H NMR (400 MHz, C₆D₆) spectrum of norbornene.



Figure S34. [KH + Mg(HMDS)₂·Et₂O] catalyzed hydrogenation of norbornene (99% yield).^[5-8]



Figure S35. [KH + Ca(HMDS)₂·(THF)₂] catalyzed hydrogenation of norbornene (99% yield).



Figure S37. [KH + Mg(HMDS)₂·Et₂O] catalyzed hydrogenation of of 1-hexene (99% conv.; 88% of n-octane and 12% of isomers).^[5-8]



Figure S38. **[KH + Ca(HMDS)**₂·(**THF)**₂**]** catalyzed hydrogenation of of 1-hexene (98% conv.; 78% of n-octane and 20% of isomers).



Figure S39. ¹H NMR (400 MHz, C₆D₆) spectrum of 1,9-decadiene.



Figure S40. **[KH + Mg(HMDS)**₂·**Et**₂**O]** catalyzed hydrogenation of 1,9-decadiene (99% conv.; 76% of n-octane and 24% of isomers).^[5]



Figure S41. [KH + Ca(HMDS)₂·(THF)₂] catalyzed hydrogenation of 1,9-decadiene (97% conv.; 61% of n-octane and 36% of isomers).



Figure S42. ¹H NMR (400 MHz, C₆D₆) spectrum of 1,3-cyclooctene.



Figure S43. [KH + Mg(HMDS)₂·Et₂O] catalyzed hydrogenation of 1,3-cyclooctene (70% conv.; 57% of cyclooctene, 13% of cyclooctane).^[10]



Figure S44. **[KH + Ca(HMDS)**₂·(**THF**)₂] catalyzed hydrogenation of 1,3-cyclooctene (87% conv.; 79% of cyclooctene, 8% of cyclooctane).

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