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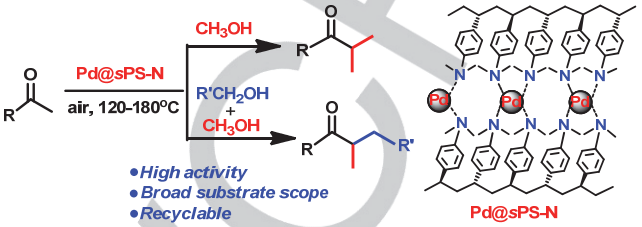
Syndiotactic Poly(aminostyrene)-Supported Palladium Catalyst for Ketone Methylation with Methanol

Lei Jiang,[a] Fang Guo,*[a] Zhenghai Shi,[a] Yang Li,*[a] and Zhaomin Hou*[a,b]

Abstract: Palladium nanoparticles immobilized in an amino-functionalized syndiotactic polystyrene (*s*PS-N) served as a novel recyclable catalyst for the dimethylation and cross methyl-alkylation of a wide range of ketones with methanol as the methylation agent. This heterogeneous catalyst (Pd@*s*PS-N) was highly robust, showing excellent thermal stability and chemical resistance. It not only showed remarkably high activity, but it could also be easily recovered by filtration without loss of activity.

The development of easily recyclable catalysts for chemical synthesis is of great importance. In this endeavor, organic polymer-supported metal nanoparticles have attracted much recent attention as high-performance heterogeneous catalysts because of their high activity, recoverability, tailorability, etc.[1] However, compared with inorganic supports, organic polymers usually show low thermal stability and poor solvent compatibility, which may therefore cause serious catalyst leaching and deactivation at high temperatures or corrosive reaction conditions. The use of crosslinked polymers[2-4] or self-assembly of heteroatom-containing polymers[5-7] with transition metals has been reported to give the polymer network-supported metal nanoparticles that could show improved thermal stability and chemical (solvent) resistance. Nevertheless, Despite these recent advances, the development of new polymer-supported, heat- and chemical- resistant metal nanoparticle catalysts remains an attractive and important research subject.

Syndiotactic polystyrene (*s*PS) is known to show high melting point, good crystallinity, and excellent resistance to heat and chemicals.[8] The use of *s*PS for the intercalation of functional molecules[9] and gold nanoparticles[10] in the semi-crystalline polymer nanopores has been previously reported. However, because of the lack of polar functional groups, the capability of *s*PS for the immobilization of recoverable active metal catalysts has been limited. We have recently achieved the synthesis of amino-functionalized syndiotactic polystyrene (*s*PS-N) by the syndiospecific polymerization of *para-N,N*-dimethylaminostyrene using a half-sandwich scandium catalyst.[8c,11] This polymer not only exhibited good thermal stability (melting point 252 °C), crystallinity, and chemical resistance originated from the unique syndiotactic polystyrene structure, but it also showed promising capability for the immobilization of palladium nanoparticles because of the presence of the functional amino groups.[11] These results prompted us to examine whether the palladium nanoparticles immobilized in *s*PS-N can serve as a recoverable catalyst for organic synthesis.



Scheme 1. Dimethylation and methyl-alkylation of ketones with methanol as the methylation agent by a novel polymerimmobilized palladium nanoparticle catalyst (Pd@*s*PS-N).

To demonstrate the potential of the *s*PS-N-immobilized palladium nanoparticles (Pd@*s*PS-N) as a useful recyclable catalyst, we selected the α-methylation of ketones with methanol because this reaction is atom-economical and environmentally benign, which generates water as the only byproduct. The C-alkylation with alcohols involving hydrogen auto-transfer reaction has received increasing attention for the construction of carbon−carbon bonds.[12] In particular, methanol is an abundant, renewable fundamental chemical feedstock, and the use of methanol as a methylation agent is of great interest and importance. However, the dehydrogenation energy of methanol (ΔH= + 84 kJ mol^{-1}) is higher than those of longer alcohols such as ethanol (ΔH = + 68 kJ mol^{-1}),[13] and therefore, the use of methanol as a C1 alkylation agent is more difficult. In 2011, Krische and coworkers reported the pioneering direct C−C coupling of methanol with allenes using a homogeneous iridium catalyst.[14] More recently, the groups of Obora,[15] Donohoe,[16] Andersson[17] and Li[18] achieved the α-methylation of ketones with methanol by using homogeneous iridium and rhodium catalysts. Despite these recent advances, a recyclable heterogeneous catalyst for the methylation of ketones with methanol has remained unknown to date, although several heterogeneous catalysts such as Ru/hydrotalcite,[19] Pd/AlO(OH),[20] Pd/C,[21] Ag/Al_2O_3,[22] and Pd/viologen-polymer[23] have been reported for C-alkylation reactions with benzyl alcohols or long chain aliphatic alcohols.

We report here our studies on the α-dimethylation and cross methyl-alkylation of ketones with methanol as the methylation agent using the *s*PS-N-immobilized palladium catalyst (Pd@*s*PS-N) (Scheme 1). We found that the palladium nanoparticle catalyst Pd@*s*PS-N not only

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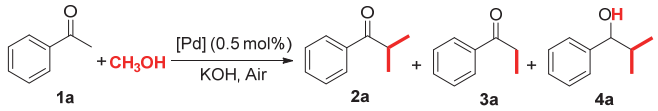
Table 1. Methylation of acetophenone with methanol by Pd catalysts[a]



Run	[Pd]	KOH [mmol]	T [°C]	T [h]	Yield [%][b]		
					2a	3a	4a
1	Pd@*s*PS-N[c]	1	90	24	4	17	0
2	Pd@*s*PS-N[c]	1	120	24	90	6	0
3	Pd@*s*PS-N[c]	2	120	12	94	2	0
4	Pd@*s*PS-N[c]	2	150	9	15	2	75
5	Pd@*s*PS[d]	1	120	24	2	17	0
6	Pd@*a*PS-N[e]	1	120	24	1	10	0
7	Pd@A21-1[f]	1	120	24	24	30	0
8	Pd/C	1	120	24	2	17	0
9	$Pd(PPh_3)_4$	1	120	24	0	7	0

[a] Reaction conditions: acetophenone (1 mmol), methanol (2 mL), [Pd] (0.005 mmol), KOH (1 or 2 mmol). [b] GC yield based on acetophenone. [c] Palladium (3 wt%) supported on syndiotactic poly(*para*-*N*,*N*-dimethylaminostyrene). [d] Palladium (3 wt%) supported on syndiotactic polystyrene. [e] Palladium (3 wt%) supported on atactic poly(*para*-*N*,*N*-dimethylaminostyrene). [f] Palladium (3 wt%) supported on Amberlyst A-21 (macroporous crosslinked polystyrene).

showed unusually high activity but it could also be easily recovered and reused, thus constituting the first example of a recyclable catalyst for C-alkylation with methanol.

At first, we examined the methylation of acetophenone with methanol as a model reaction in the presence of Pd@*s*PS-N (0.5mol %) and KOH (1 equiv.) under air (Table 1). At 90 °C the reaction was not efficient, which gave a mixture of the dimethylation and monomethylation products **2a** and **2b** in 4% and 17% yields, respectively in 24 h (Table 1, Run 1). When the reaction was carried out at 120 °C, the dimethylation product **2a** was obtained in 90% yield together with 6% of the monomethylation product **3a** (Table 1, Run 2). The use of 2 equiv. of KOH further promoted the reaction, affording **2a** in 94% yield in 12 h (Table 1, Run 3). The reaction at further higher temperature (150 °C) led to hydrogenation of the carbonyl group and gave the dimethylated alcohol product **4a** as a major product (75%) (Table 1, Run 4). For comparison, various related palladium catalysts were also examined. In sharp contrast, the analogous amino-free syndiotactic polystyrene- (Pd@*s*PS, Table 1, Run 5), atactic poly(*para*-*N*,*N*-dimethylaminostyrene)- (Pd@*a*PS-N, Table 1, Run 6), or commercially available Amberlyst A-21 (crosslinked polystyrene containing dimethylamino group)- (Pd@A21, Table 1, Run 7) supported palladium catalyst showed much lower activity under the same conditions. The commercially available heterogeneous Pd/C catalyst did not work well for the present methylation of acetophenone with methanol (Table 1, Run 8), though it showed good activity for the alkylation of ketones with higher alcohols.[21] The typical homogeneous palladium catalyst $Pd(PPh_3)_4$ gave the monomethylation product **3a** in 7% yield, while the dimethylation product **2a** was not observed under the same conditions (Table 1, Run 9); note that precipitation of palladium black occurred in a few hours. These results clearly demonstrate that the syndiotactic poly(*N*,*N*-dimethylaminostyrene) is a unique platform for the immobilization of highly active palladium nanoparticle catalyst.

The transmission electron microscope (TEM) analysis of Pd@*s*PS-N revealed that spherical palladium nanoparticles with a diameter of 2-3 nm were uniformly dispersed in the *s*PS-N matrix (Figs. 1a and 1b). In contrast, the Pd nanoparticles in Pd@*s*PS, and Pd@*a*PS-N were significantly aggregated (Figs. 1e and 1f). These results suggest that both the amino functional group and the syndiotactic structure of *s*PS-N should play an important role in preventing the in-situ generated palladium nanoparticles from aggregation. At room temperature, the Pd morphology and distribution in Pd@*s*PS-N and Pd@A-

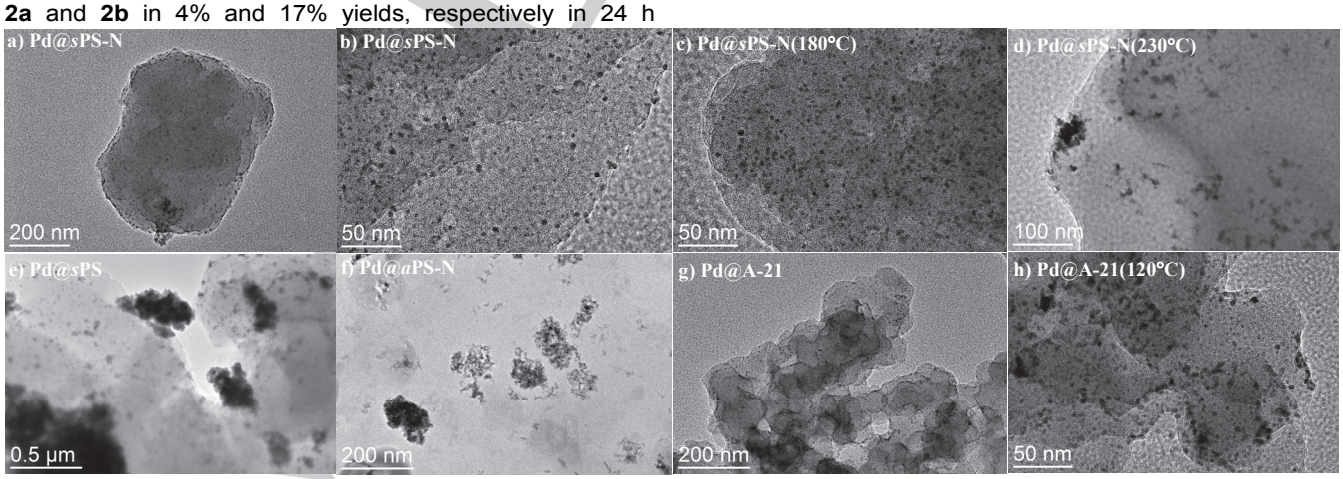


Figure. 1 TEM images. **a**) and **b**) Pd@*s*PS-N (original), **c**) and **d**) Pd@*s*PS-N after being heated at 180 °C and 230 °C, respectively in toluene for 2 days, **e**) Pd@*s*PS (original), **f**) Pd@*a*PS-N (original), **g**) Pd@A-21 (original), **h**) Pd@A-21 after being heated at 120 °C in toluene for 1 day.

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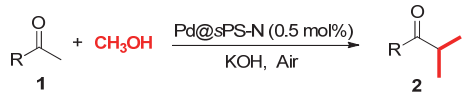
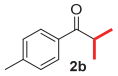
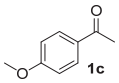
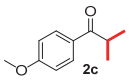
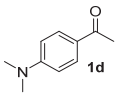
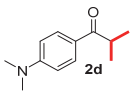
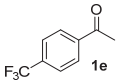
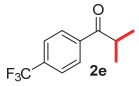
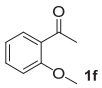
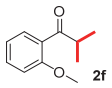
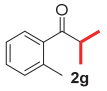
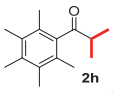
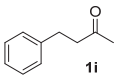
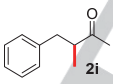
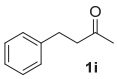
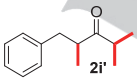
Table 2. Methylation of various ketones with methanol by Pd@*s*PS-N[a]



Run	Ketone	T [°C]	KOH [mmol]	t [h]	Product	Yield [%][b]
1		120	2	16		86
2		150	3	11		89
3		180	3	10		75
4		120	2	3		68
5		120	2	8		90
6		120	1	20		96
7		180	3	6		97
8		120	2	2		62
9		120	2	48		80
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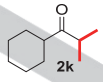
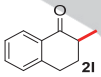
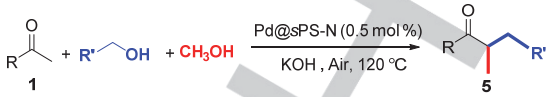
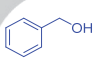
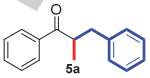
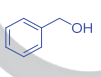
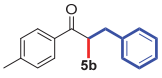
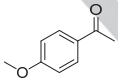
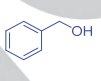
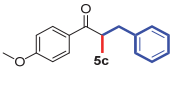
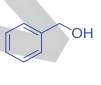
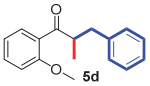
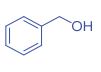
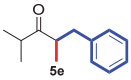
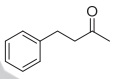
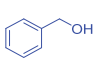
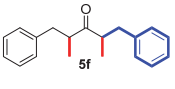
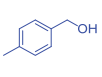
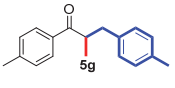
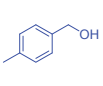
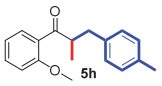
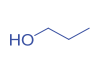
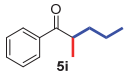
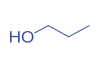
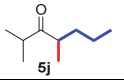
11		150	3	30		78
12		120	2	10		94
13		120	2	16		87

[a] Reaction conditions: ketone (1 mmol), methanol (2 mL), [Pd] (0.005 mmol), KOH. [b] All yields are isolated yields.

Table 3. Pd@*s*PS-N-catalyzed three component methyl-alkylation reaction of various ketones with methanol and higher alcohols[a]



Run	Ketone	Alcohol	T [h]	Product	Yield [%][b]
1			8		86
2			10		91
3			10		91
4			8		87
5			6		95
6			10		88
7			10		92
8			8		91
9[c]			2, 15		69
10[d]			3, 48		57

[a] Reaction conditions: ketone (1.25 mmol), methanol (2 mL), alcohol (1.0 mmol), [Pd] (0.005 mmol), KOH (2.0 mmol), 120 °C, unless otherwise noted. [b] All yields are isolated yields. [c] After the reaction of ketone (1.0 mmol) with propanol (5.0 mmol) and KOH (1.0 mmol) was carried out for 2 h, another portion of KOH (1.0 mmol) and methanol (2 mL) were added, further reacted for 15 h. [d] After the reaction of ketone (1.0 mmol) with propanol (10.0 mmol) and KOH (2.0 mmol) was carried out for 3 h, another portion of KOH (2.0 mmol) and methanol (2 mL) were added, further reacted for 48 h.

21 were similar to each other (Figs. 1a and 1g). On heating at 120 °C, the size of the Pd nanoparticles in Pd@A-21 significantly increased (Fig. 1h). In sharp contrast, the size and the uniform distribution of the palladium nanoparticles in Pd@*s*PS-N remained almost unchanged even after being heated at 180 °C for two days (Fig. 1c). At 230 °C, which is close to the melting point of *s*PS-N (252 °C), the Pd nanoparticles in Pd@*s*PS-N began to aggregate (Fig. 1d). The unusual robustness of the Pd nanoparticles in Pd@*s*PS-N may result from the unique interplay of the dimethylamino functional groups and the syndiotactic polystyrene structures[10] as well as the excellent thermal stability and chemical resistance of the *s*PS-N polymer which may therefore effectively prevent the palladium nanoparticles from aggregation or leaching. This could

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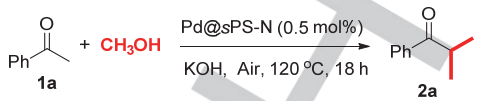
account for the unusually high activity of Pd@*s*PS-N compared to other related catalysts under the present reaction conditions (Table 1).

The dimethylation of various ketones with methanol was then examined by using the Pd@*s*PS-N catalyst. Some representative results are shown in Table 2. Acetophenones having either electron-donating (such as OMe and NMe_2) or electron-withdrawing (such as CF_3) groups at the phenyl ring were all suitable for this reaction, selectively affording the dimethylation products in high yields (Table 2, Runs 1−4). Substituents at the ortho positions of the carbonyl group did not hamper the high reaction efficiency (Table 2, Runs 5−7). In the case of 4-phenyl-2-butanone (**1i**), the reaction at 120 °C for 2 h gave selectively the methylene monomethylation product **2i** in 62% yield (Table 2, Run 8), while the reaction for a longer time (48 h) led to methylation at both the methylene unit and the methyl group, affording the trimethylation product **2i'** in 80% yield (Table 2, Run 9). These results suggest that the methylene unit is more reactive than the methyl group. Methyl isopropyl ketone (**1j**) and methyl cyclohexyl ketone (**1k**) exclusively underwent dimethylation at the methyl group, affording **2j** and **2k**, respectively in high yields (Table 2, Runs 10 and 11). The methylation of benzocyclohexanone (**1l**) and cyclohexanone (**1m**) was also efficiently achieved, giving **2l** and **2m**, respectively in high yields (Table 2, Runs 12 and 13). It is also worth noting that all of these reactions could be carried out under air with a catalyst loading as low as 0.5 mol %.

The present methylation of ketones with methanol may possibly proceed according to a reaction pathway reported previously.[15,16a,17] The dehydrogenation of methanol by the Pd nanoparticles in Pd@*s*PS-N could result in formation of formaldehyde and a Pd–hydride species, which is a key step in the process of ketone alkylation. Base-catalyzed cross-aldol condensation of formaldehyde with a ketone would produce an α,β-unsaturated ketone, which could be quickly reduced by the Pd–hydride species to give the α-methylated product and regenerate the Pd nanoparticles (See Scheme S1, ESI†).

With the success of the methylation of a wide range of ketones with methanol, we then examined the three-component cross methyl-alkylation reactions of ketones with methanol and higher alcohols. Some representative results are given in Table 3. The cross methyl-benzylation of various ketones in the coexistence of methanol and benzyl alcohols selectively took place in the presence of Pd@*s*PS-N (0.5 mol % Pd) under air, affording the mixed multi-substituted ketone products **5a−h** in 86−95% yields (Table 3, Runs 1−8). The gas chromatography monitoring confirmed that the reaction occurred sequentially first by alkylation with a benzyl alcohol followed by methylation with methanol, probably because of the higher activity of benzyl alcohol than that of methanol (Table S1, ESI†). These results also demonstrate that the Pd@*s*PS-N catalyst can distinguish a benzyl alcohol from methanol under their coexistence despite its high catalytic activity. In the reaction of propanol and methanol with ketones, a stepwise feeding of propanol and methanol was needed to selectively achieve the mixed propyl-methylation, but the reaction could still be run in a "one-pot" fashion (Table 3, Runs 9 and 10).

Table 4. Pd@*s*PS-N recycling for the dimethylation of acetophenone with methanol[a]



Use	1	2	3	4	5
2a yield [%][b]	95	93	97	92	91

[a] Reaction conditions: acetophenone (3.0 mmol), methanol (6.0 mL), [Pd] (0.015 mmol), KOH (6.0 mmol). [b] GC yield based on acetophenone.

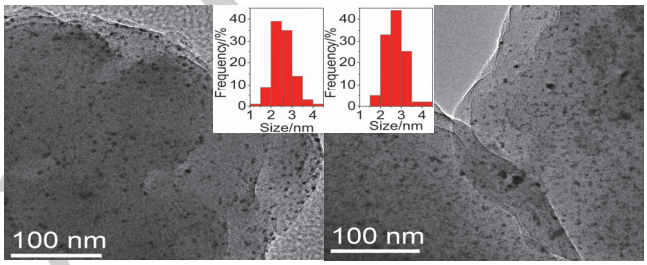


Figure 2. TEM images of Pd@sPS-N: a) original (b) after fifth reuse.

To examine the recyclability of the Pd@*s*PS-N catalyst a 3 mmol scale reaction of acetophenone (**1a**) with methanol was carried out by using the original and the recovered catalysts (Table 4). After the first reaction, which gave the dimethylation product **2a** in 95% yield, the catalyst was recovered simply by filtration without need of centrifugation. The recovered of catalyst was repeatedly used in five cycles without significant the activity (91−97% yields of **2a**). Catalyst leaching or palladium metal aggregation was almost negligible (see Figure 2 and Table S2, ESI†). These results suggest that the palladium nanoparticles in Pd@*s*PS-N are highly robust.

In summary, we have demonstrated that the palladium nanoparticles supported in a syndiotactic poly(*para-N,N*-dimethylaminostyrene) polymer (Pd@*s*PS-N) can serve as an excellent catalyst for the α-alkylation of a wide range of ketones with alcohols (including the less reactive methanol) as the alkylation agents. The reaction can be carried out under air without using an extra solvent. The immobilized palladium nanoparticle catalyst Pd@*s*PS-N is highly robust, showing excellent thermal stability and chemical resistance. It not only exhibited the highest TON (TOF) ever reported for ketone alkylation with methanol, but it can also be easily recovered and reused. The unusually high performance of

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the Pd@*s*PS-N catalyst may result from the interplay of the functional dimethylamino groups, the unique syndiotactic polymer structure, and the excellent heat and chemical resistance of the *s*PS-N polymer support, which may effectively prevent the leaching and aggregation of the palladium nanoparticles. Studies on the application of the palladium nanoparticle catalyst Pd@*s*PS-N to other chemical transformations as well as on the use of functionalized syndiotactic polystyrenes for immobilization of other metal catalysts are currently under progress.

Experimental Section

All reactions were carried out under air atmosphere and reagent without further purification. Related experiment detail and analysis can be seen in the Supporting Information.

Acknowledgements

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Keywords: alkylation • ketone • methanol • palladium • polymer-supported catalyst

[1] Typical Reviews of organic polymer-supported metal nanoparticles: a) R. Akiyama, S. Kobayashi, *Chem. Rev.* **2009**, *109*, 594–642; b) J. Lu, P. H. Toy, *Chem. Rev.* **2009**, 109, 815–838; c) S. Sarkar, E. Guibal, F. Quignard, *J. Nanopart. Res.* **2012**, *14*, 715-739; d) L. M. Bronstein, Z. B. Shifrina, *Chem. Rev.* **2011**, *111*, 5301–5344.

[2] Crosslinked polystyrene containing alcohol and epoxy moieties: a) K. Okamoto, R. Akiyama, H. Yoshida, T. Yoshida, S. Kobayashi, *J. Am. Chem. Soc.* **2005**, *127*, 2125–2135; b) Kobayashi, H. Miyamura, R. Akiyama, T. Ishida, *J. Am. Chem. Soc.* **2005**, *127*, 9251–9254; c) R. Nishio, M. Sugiura, S. Kobayash, *Org. Lett.* **2005**, *22*, 4831–4834; d) H. Hagio, M. Sugiura, S. Kobayash, *Org. Lett.* **2006**, *3*, 375–378; e) M. Takeuchi, R. Akiyama, S. Kobayashi, *J. Am. Chem. Soc.* **2005**, *127*, 13096–13097; f) W. Yoo, H. Miyamura, S. Kobayashi, *J. Am. Chem. Soc.* **2011**, *133*, 3095–3103; g) S. T. Yasukawa, H. Miyamura, S. Kobayashi, *J. Am. Chem. Soc.* **2012**, *134*, 16963–16966; h) H. Miyamura, S. Kobayashi, *Acc. Chem. Res.* **2014**, *47*, 1054−1066.

[3] Crosslinked polystyrene containing divinylbenzene: a) J. K. Cho, R. Najman, T. W. Dean, O. Ichihara, C. Muller, M. Bradley, *J. Am. Chem. Soc.* **2006**, *128*, 6276–6277; b) H. Kaur, D. Shah, U. Pa, *Catal. Commun.* **2011**, *12*, 1384–1388; c) A. K. Shil, S. Kumar, C. B. Reddy, S. Dadhwal, V. Thakur, P. Das, *Org. Lett.* **2015**, *17*, 5352−5355.

[4] Crosslinked polyethylene: a) P. Liu, Z. Dong, Z. Ye, W. Wang, B. Li, *J. Mater. Chem. A* **2013**, *1*, 15469–15478; b) P. Liu, Z. Ye, W. Wang, B. Li, *Macromolecules* **2013**, *46*, 72−82.

[5] Polyacrylamides: a) S. M. Sarkar, Y. Uozumi, Y. M. A. Yamada, *Angew. Chem. Int. Ed.* **2011**, *50*, 9437–9441; *Angew. Chem.* **2011**, *123*, 9609–9613; b) Y. M. A. Yamada, S. M. Sarkar, Y. Uozumi, *J. Am. Chem. Soc.* **2012**, *134*, 9285−9290; c) Y. M. A. Yamada, S. M. Sarkar, Y. Uozumi, *J. Am. Chem. Soc.* **2012**, *134*, 3190−3198.

[6] Polypyrrole: a) V. A. Zinovyeva, M. A. Vorotyntsev, L. Bezverkhyy, D. Chaumont, J. C. Hierso, *Adv. Funct. Mater.* **2011**, *21*, 1064–1075; b) S. K. Mahato, R. U. Islam, C. Acharya, M. J. Witcomb, K. Mallick, *ChemCatChem* **2014**, *6*, 1419–1426.

[7] Polyaniline: a) B. J. Gallon, R. W. Kojima, R. B. Kaner, P. L. Diaconescu, *Angew. Chem. Int. Ed.* **2007**, *46*, 7251–7254; *Angew. Chem.* **2007**, *119*, 7389–7392; b) J. Han, Y. Liu, R. Guo, *J. Am. Chem. Soc.* **2009**, *131*, 2060–2061; c) L. Yu, Y. P. Huang, Z. Wei, Y. H. Ding, C. L. Su, Q. Xu, J. *Org. Chem.* **2015**, *80*, 8677−8683.

[8] a) N. Tomotsu, N. Ishihara, T. H. Newman, M. T. Malanga, *J. Mol. Catal A: Chem.* **1998**, *128*, 167–190; b) M. Malanga, *Adv. Mater.* **2000**, *12*, 1869–1872; c) Y. Luo, J. Baldamus, Z. Hou, *J. Am. Chem. Soc.* **2004**, *126*, 13910–13911.

[9] a) Y. Uda, F. Kaneko, N. Tanigaki, T. Kawaguchi, *Adv. Mater.* **2005**, *17*, 1846–1850; b) C. Daniel, C. Rufolo, F. Bobba, A. Scarfato, A. M. Cucolo, G. Guerra, *J. Mater. Chem.* **2011**, *21*, 19074–19079; c) P. Rizzo, T. Monte-fusco, G. Guerra, *J. Am. Chem. Soc.* **2011**, *133*, 9872–9877.

[10] a) A. Buonerba, C. Cuomo, S. O. Sánchez, P. Canton, A. Grassi, *Chem Eur. J.* **2012**, *18*, 709–715; b) A. Buonerba, A. Noschese, A. Grassi, *Chem. Eur. J.* **2014**, *20*, 5478–5486; c) A. Noschese, A. Buonerba, P. Canton, S. Milione, C. Capacchione, A. Grassi, *J. Catal.* **2016**, *340*, 30–40.

[11] Z. Shi, F. Guo, Y. Li, Z. Hou, *J. Polym. Sci., Part A: Polym. Chem.* **2015**, *53*, 5–9.

[12] Reviews of alkylation of ketones with alcohols: a) Y. Obora, *Top. Curr. Chem.* **2016**, *374*, 11–40; b) Y. Obora, *ACS Catal.* **2014**, *4*, 3972–3981; c) G. E. Dobereiner, R. H. Crabtree, *Chem. Rev.* **2010**, *110*, 681–703; d C. Gunanathan, D. Milstein, *Science* **2013**, *341*, 1229712–1229723; e) Q. Yang, Q. Wang, Z. Yu, *Chem. Soc. Rev.* **2015**, *44*, 2305–2329; f) S. Pan, T. Shibata, *ACS Catal.* 2013, 3, 704–712.

[13] a) M. Qian, M. A. Liauw, *G. Emig, Appl. Catal. A-Gen.* **2003**, *238*, 211–222; b) W. Lin, H. Chang, *Catal. Today.* **2004**, *97*, 181–188.

[14] J. Moran, A. Preetz, R. A. Mesch, M. J. Krische, *Nat. Chem.* **2011**, *3*, 287–290.

[15] S. Ogawa, Y. Obora, *Chem. Commun.* **2014**, *50*, 2491–2493.

[16] L. Chan, D. L. Poole, D. Shen, M. P. Healy, T. J. Donohoe, *Angew. Chem. Int. Ed.* **2014**, *53,* 761–765; *Angew. Chem.* **2014**, *126*, 780–784; b) J. R. Frost, C. B. Cheong, W. M. Akhtar, D. F. Caputo, N. G. Stevenson, T. J. Donohoe, *J. Am. Chem. Soc.* **2015**, *137*, 15664–15667; c) D. Shen, D. L. Poole, C. C. Shotton, A. F. Kornahrens M. P. Healy, T. J. Donohoe, *Angew. Chem. Int. Ed.* **2015**, *54*, 1642–1645; *Angew. Chem.* **2015**, *127*, 1662–1665.

[17] X. Quan, S. Kerdphon, P. G. Andersson, *Chem. Eur. J.* **2015**, *21*, 3576–3579.

[18] F. Li, J. Ma, N. Wang, *J. Org. Chem.* **2014**, *79*, 10447–10455.

[19] K. Motokura, D. Nishimura, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* **2004**, *126,* 5662–5663.

[20] M. S. Kwon, N. Kim, S. H. Seo, I. S. Park, R. K. Cheedrala, J. Park, *Angew. Chem. Int. Ed.* **2005**, *44*, 6913–6915; *Angew. Chem.* **2005**, *117* 7073–7075.

[21] C. Cho, *J. Mol. Catal. A-Chem.* **2005**, *240*, 55–60.

[22] K. Shimizu, R. Sato, A. Satsuma, *Angew. Chem. Int. Ed.* **2009**, *48*, 3982–3986; *Angew. Chem.* **2009**, *121*, 4042–4046.

[23] Y. M. A. Yamada, Y. Uozumi, *Org. Lett.* **2006**, *8*, 1375–1378.

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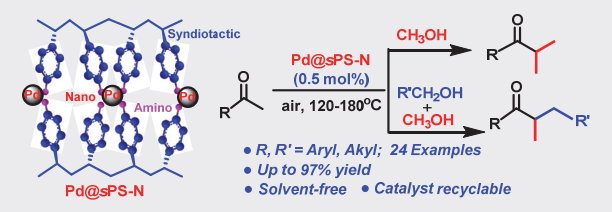

A novel recyclable and highly active catalyst (Pd@*s*PS-N) for the methylation and methyl-alkylation of a wide range of commercially accessible ketones with methanol as the methylation agent was established by immobilization of palladium nanoparticles on a unique amino-functionalized syndiotactic polystyrene.

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Syndiotactic Poly(aminostyrene)-Supported Palladium Catalyst for Ketone Methylation with Methanol

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