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Supporting Information

for

Nitration of Alkanes with Nitric Acid by Vanadium-Containing Polyoxometalates as Catalyst Precursors

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Table S1. Nitration of various alkanes catalyzed by $[VO(H_2O)_5]H[PMo_{12}O_{40}]$ with nitric acid[a]

entry	substrate	conditions	TTON[b]	products	yield/ %
1	adamantane	**I**	160	1-nitroadamantane	54
				1,3-dinitroadamantane	7
				1-adamantanol	27
				2-adamantanone	5
2	1,3-dimethyladamantane	**I**	114	1,3-dimethyl-5-nitroadamantane	56
				3,5-dimethyl-1-adamantanol	38
3	1-chloroadamantane	**I**	108	1-chloro1-3-nitroadamantane	36
				3-chloro-1-adamantanol	33
4	cyclohexane	**II**	40	nitrocyclohexane	10
				cyclohexanol	1
5	cyclooctane	**I**	100	nitrocyclooctane	25
				dinitrocyclooctanes	14
				cyclooctanone	11
6	toluene	**II**	168	(nitromethyl)benzene	20
				benzyl alcohol	12
				benzaldehyde	15
7	*m*-xylene	**II**	320	1-methyl-3-(nitromethyl)benzene	35
				m-tolualdehyde	18
8	*p*-xylene	**II**		1-methyl-4-(nitromethyl)benzene	30
				p-tolualdehyde	33

[a] Reaction conditions **I**: Alkane (1 mmol), $[VO(H_2O)_5]H[PMo_{12}O_{40}]$ (1.67 mM, 0.5 mol%), nitric acid (2 mmol), acetic acid (3 mL), 356 K, under 1 atm of argon. Yields were based on alkane and determined by GC using naphthalene as an internal standard. Reaction conditions **II**: Alkane (18.5 mmol), $[VO(H_2O)_5]H[PMo_{12}O_{40}]$ (1.00 mM, 0.03 mol%), nitric acid (2 mmol), acetic acid (3 mL), 356 K, under 1 atm of argon. Yields were based on nitric acid used and determined by GC using naphthalene as an internal standard. [b] TTON (total turnover number) = products (mol)/ $[VO(H_2O)_5]H[PMo_{12}O_{40}]$ used (mol).

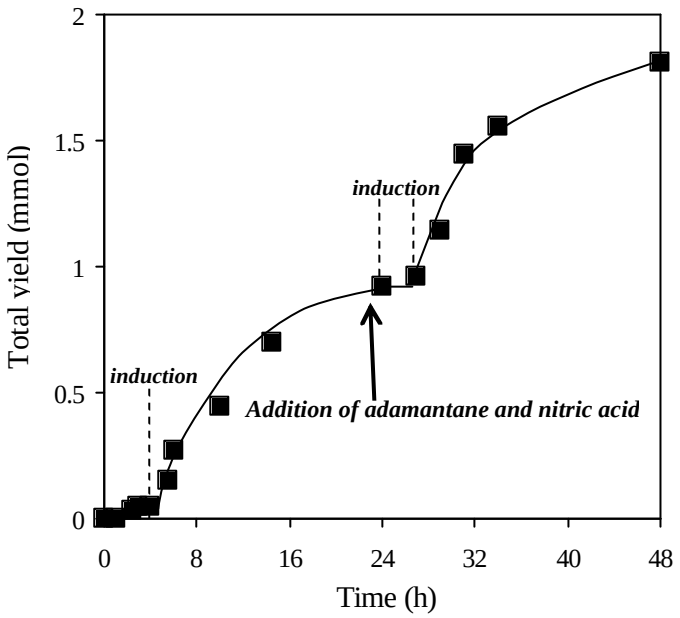


Figure S1. Reaction profiles of the nitration of adamantane with nitric acid catalyzed by $H_4PVMo_{11}O_{40}$. Reaction conditions were as follows: Adamanatane (1 mmol), $H_4PVMo_{11}O_{40}$ (0.5 mol%, 1.67 mM), nitric acid (2 mmol), acetic acid (3 mL), 356 K, under 1 atm of argon. After 24 h, adamantane (1 mmol) and nitric acid (2 mmol) were again added to the reaction solution. An arrow indicates the addition of adamantane and nitric acid.

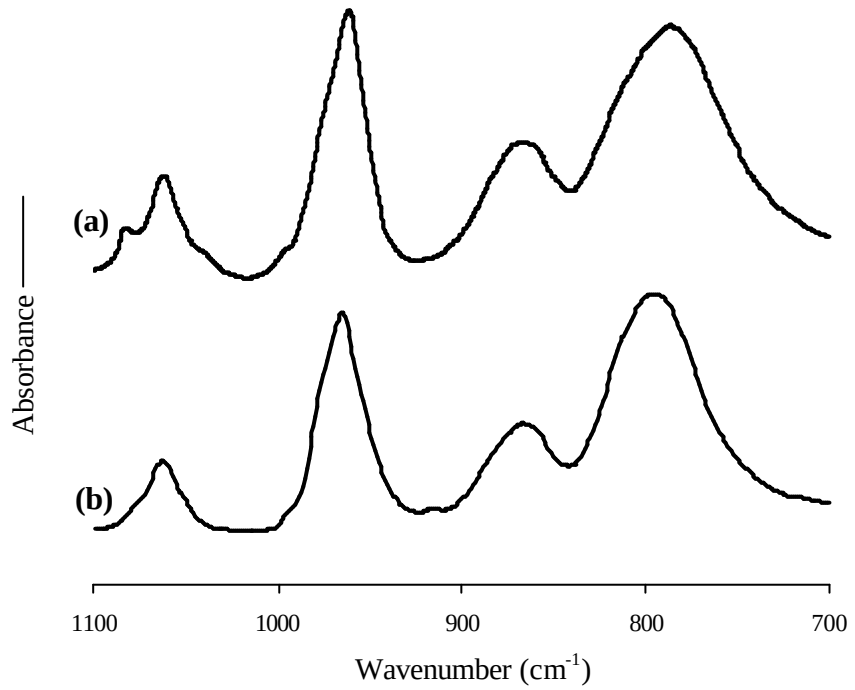
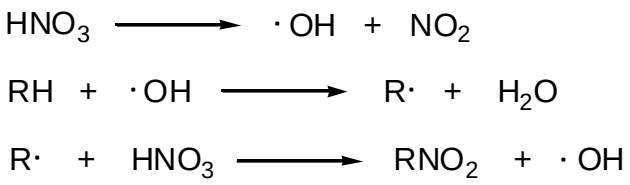


Figure S2. IR spectra of (a) fresh $H_4PVMo_{11}O_{40}$ and (b) recovered catalysts (as a Cs salt). The catalyst was recovered after the treatment with adamantane in acetic acid at 356 K for 4 h under 1 atm of argon.



Scheme S1.