

High Catalytic Efficiency of Nanostructured Molybdenum Trioxide in the Benzylolation of Arenes and an Investigation of the Reaction Mechanism

Feng Wang^{*[a, b]} and Wataru Ueda^{*[b]}

Abstract: The synthesis and characterization of nanostructured MoO₃ with a thickness of about 30 nm and a width of about 450 nm are reported. The composition formula of the MP (precipitation method) precursor was estimated to be [(NH₄)₂O]_{0.169}·MoO₃·(H₂O)_{0.239}. The calcination of the precursor in air afforded nanostructured pellets of the α-MoO₃ phase. The nanostructured MoO₃ catalyst exhibited high efficiency in catalyzing the benzylolation of various arenes with substituted benzyl alcohols, which were strikingly different to common bulk MoO₃. Most reactions offered >99% conversion and >99% selectivity to mono-

alkylated compounds. MoO₃ is a typical acid catalyst. However, the benzylolation reaction over nanostructured MoO₃ does not belong to the acid-catalyzed type or defect site-catalyzed type, since the catalyst has no acidity and defect site on surface. Characterization with thermal, spectroscopic, and electronic techniques reveal that the catalyst contains fully oxygen-coordinated MoO₆ octahedrons on the surface but partial-

ly reduced species (Mo⁵⁺) within the bulk phase. The terminal oxygen atoms of Mo=O bonds on the (010) basal plane resemble oxygen anion radicals and act as active sites for the adsorption and activation of benzyl alcohols by electrophilic attack. Such sites are indispensable for catalytic reactions since the blocking of these sites by electron acceptors, such as tetracyanoethylene (TCNE), can greatly decrease catalytic activity. This work represents a successful example of combining a heterogeneous catalysis study with nanomaterial synthesis.

Keywords: benzylolation • heterogeneous catalysis • molybdenum trioxide • molybdenum • nanostructures • surface chemistry

Introduction

Molybdenum oxide is widely used in catalysts, sensors, lubricants, and fuel cell materials. Specifically, the catalysis of MoO₃ greatly relies on the crystal phase, surface structure, and particle size. To develop a highly active and selective catalyst, it is necessary to couple the synthesis of a nanostructured material with the understanding of material surface structures, like local geometry and electronic properties of active sites.^[1] Regarding the synthesis, a variety of tech-

niques has been developed to control the architectures and morphological patterns of molybdenum oxide. Examples include hydrothermal synthesis, template or host molecule-involved synthesis, and electrochemical processes. The morphologies of rods,^[2–4] wires,^[5] tubes,^[6] belts,^[7,8] ribbons,^[9] rings,^[10] have been prepared. However, little attention was paid to catalytic performance. A search we undertook through the SciFinder Scholar database (keyword: molybdenum oxide) returned more than 20000 papers, most of which were devoted to material synthesis. Regarding the surface science, research on the structure of bulk MoO₃ with perfect crystalline phase by microscopy,^[11] spectroscopy,^[12,13] and calculations^[14–17] has provided significant insight into the atomic surface chemistry governing the catalytic activity.

Bulk MoO₃ is known to be catalytically inactive. Much research has focused on Mo-based complex oxide catalysts. In combination with other elements, such as bismuth, vanadium, cobalt, or aluminum, Mo-based catalysts can be active and selective for many reactions. Selective oxidation,^[18–21] hydrogenation, and dehydrogenation^[22–24] are a few examples of important applications of these catalysts. The general character of Mo-catalyzed reactions is that certain reaction

[a] Dr. F. Wang
CREST, Japan Science and Technology Corporation (CREST-JST)
Kawaguchi, Saitama 332-0012 (Japan)
Fax: (+81) 11-706-9164
E-mail: wangfeng@cat.hokudai.ac.jp

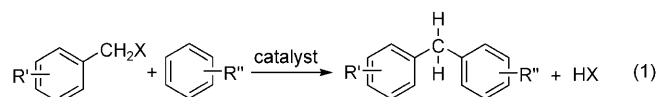
[b] Dr. F. Wang, Prof. Dr. W. Ueda
Catalysis Research Center, Hokkaido University, N-21, W-10
Sapporo 001-0021 (Japan)
Fax: (+81) 11-706-9164
E-mail: ueda@cat.hokudai.ac.jp

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steps need oxygen species from the catalyst surface or the transfer of hydrogen species to the catalyst surface.^[25] In the complicated system, the supports or co-catalysts play a key role in providing high specific surface area and additional acidity or basicity. Thus, the real role of MoO₃ in catalysis is difficult to investigate. Furthermore, it is known that MoO₃ can exhibit pronounced crystallographic anisotropy. As a result, different exposed crystal facets have different catalytic behaviors (so-called structure sensitivity).^[26] Despite many efforts in experiments and calculations, the active facet of MoO₃ still remains debatable.^[27,28] Therefore, pure nanostructured MoO₃ is more favorable than complex oxides for studying active site and sensitive facets given that MoO₃ is active and selective.

Nanostructured oxides, compared to their bulk counterparts, can exhibit unexpected catalysis. Some examples are MgO,^[29–33] CeO₂,^[34] TiO₂,^[35] and WO₃.^[36] The active site of these catalysts is typically an oxygen vacancy or a defect center. To the best of our knowledge, there has been no report on utilizing nanostructured MoO₃ in a catalytic reaction. Recently, we found that the nanostructured MoO₃ consisting of unsupported platelets exhibits excellent catalytic activities in benzylation reactions.^[37] By treating benzyl alcohol in toluene with a catalytic amount of nanostructured MoO₃, we obtained benzyl toluene isomers in a quantitative yield. Benzylation is a traditional and very important Friedel–Crafts alkylation reaction and represents a satisfactory route to synthesize diphenylmethane derivatives [Eq. (1)].^[38] In comparison with processes using H₂SO₄, AlCl₃, metal complexes,^[39–41] supported solid acids,^[42,43] metal ion-incorporated zeolite catalysts,^[44] complex oxides,^[45,46] and Nafion membranes,^[47] our method possesses the advantages of facile catalyst preparation, excellent catalytic performances and easy catalyst recycling and reuse.

Herein, we will demonstrate that nanostructured MoO₃ containing oxygen-saturated MoO₆ octahedrons on the surface, which is strikingly different to common bulk MoO₃, is



high efficient at catalyzing the benzylation of various arenes with substituted benzyl alcohols. Most reactions offer >99% conversion and >99% selectivity to monoalkylated compounds. More interestingly, the reaction is not catalyzed by defect sites, since the surface is defect-free. Moreover, the reaction is not catalyzed by acid sites, since nanostructured MoO₃ contains no acid sites. We will show that the terminal oxygen of the Mo=O bond on the (010) basal plane, which resembles an anion radical, is the active site for the adsorption and activation of substrate. Although the catalysis of an oxygen anion radical has been previously discussed on complex oxides,^[48] such phenomena and the excellent efficiency in catalysis is completely new for a nanostructured material like MoO₃. The present research will contribute considerably to the understanding of the surface of the nanomaterial and its heterogeneous catalysis.

Results and Discussion

Several MoO₃ catalysts were prepared and these samples are designated as follows: MP, precipitation method; MH, hydrothermal method; MM, calcination of molybdate salt; and MC, commercial product. All catalysts were tested in the benzylation of toluene with benzyl alcohol. The results of the reactions are listed in Table 1. The reaction does not occur when the catalyst is not present (Table 1, entry 1). The commercial MoO₃ (MC-MoO₃, Table 1, entry 2), the MM (Table 1, entry 3) and the MH (Table 1, entry 4) catalyzed the reaction to give the desired product, but also produced benzyl diether (BDE) as a byproduct. In contrast, the MP catalyst gave the best results (Table 1, entries 5, 6), with

Table 1. Alkylation of toluene over molybdenum oxides.^[a]

Entry	Cat ^[b]	Color	Crystal system ^[c]	S ^[d] [m ² g ^{−1}]	Crystallite size [nm] ^[e]			t [min]	Conv. [%] ^[f]	Major product		BDE [%] ^[j]
					020	110	021			Sel. [%] ^[g]	IY [%] ^[h]	
1	–	–	–	–	–	–	–	30	0	–	–	–
2	MC-MoO ₃	light gray	orth	2.9	94.7	91.6	102.0	30	54	44:9:47	–	26
3	MM	light gray	orth	6.5	48.7	29.1	81.9	40	90	44:9:47	–	10
4	MH	white	orth	7.7	44.3	26.8	78.4	30	82	44:14:42	–	5
5	MP	light blue	orth	14.6	41.0	24.3	70.7	10	76	44:10:46	–	0
6								20	>99	44:10:46	95	0
7								30	>99	44:10:46	–	0
8	[i]							30	>99	44:10:46	93	0
9	[k]							20	>99	44:8:48	92	0
10	MP-NC	dark blue	orth + mono	17.0	35.6	20.2	48.1	30	0	–	–	–
11	MM-m15	light gray	orth	20.5	34.0	18.5	45.6	40	98	46:7:47	–	42
12	β-MoO ₃	bright yellow	mono	21.5	–	–	–	60	0	–	–	–
13	MC-MoO ₂	brown	mono	2.0	–	–	–	260	11	48:6:46	–	55

[a] Alcohol 0.24 mL, arene 15.0 mL, hexadecane (internal standard) 0.1 mL, reaction temperature 110 °C, catalyst 0.3 g, Ar protection. [b] MP: precipitation method; MH: hydrothermal method; MM: calcination of molybdate salt; MC: commercial product. [c] orth: orthorhombic; mono: monoclinic. [d] Specific surface area by N₂ adsorption (BET method). [e] Calculated by Sherrer's formula. [f] GC conversion of benzyl alcohol. Isomeric ratio of *o*:*m*:*p*. [h] Yield of isolated product. [i] The selectivity of benzyl diether determined by the integration of GC peak area. [j] Catalyst results over different batch of catalyst MP. [k] PhCH₂Cl was alkylating agent.

>99% conversion of benzyl alcohol and a 95% yield of the isolated alkylated product in 20 min at 110°C (heated to reflux in toluene). The regioselectivity was maintained at 44:10:46 (*ortho:meta:para*). Extending the reaction time to 30 min did not lead to any byproduct (Table 1, entry 7), such as polymer.^[49] Different batches of catalysts gave very similar results (Table 1, entry 8), suggesting that the catalyst preparation can be reproduced. Similar good results employing benzyl chloride as the alkylating agent to benzyl alcohol were achieved over the MP catalyst (Table 1, entry 9). Because of less poisoning and easy handling, benzyl alcohol was preferred to benzyl chloride in this research. The sample calcined in a N₂ atmosphere (MP-NC, Table 1, entry 10) was totally inactive in the 30 min reaction. The milling of MM, intended to increase the surface area of MM, resulted in higher conversion but worse selectivity compared to unmilled MM (Table 1, entry 11). Although β -MoO₃ was claimed to be an active catalyst in selective oxidation, the catalyst was totally inactive in alkylation (Table 1, entry 12). The catalysis over MoO₂ is sluggish and less selective (Table 1, entry 13).

After the reaction, the MP catalyst was filtered off, washed with toluene, and reused several times. As a result, the conversions and product distributions over the reused catalyst were comparable to fresh MP (Figure S1 in the Supporting Information). Removal of the MP catalyst in the course of the reaction completely stopped the conversion of benzyl alcohol, and the addition of the catalyst clearly triggered the reaction (Figure 1), suggesting that the reaction was heterogeneously catalyzed. The inductively couple plasma (ICP) mass analysis revealed that no Mo species leached into the reaction mixture.

Having established the method of the benzylation of toluene, we were interested in the alkylation of other substituted arenes with benzyl alcohol (Table 2) over the MP catalyst. As expected, a variety of electron-rich arenes, such as anisole (Table 2, entry 2, yield 94%), *p*-xylene (Table 2, entry 3, yield 93%), ethylbenzene (Table 2, entry 4, yield 93%), and mesitylene (Table 2, entry 5, yield 95%) gave the corresponding benzylated arenes in excellent yield. Due to the activated benzene ring in anisole, the benzylating reaction primarily occurred in *para* and *ortho* positions to the methoxy group. For entries 3–5 in Table 2, these reactions were

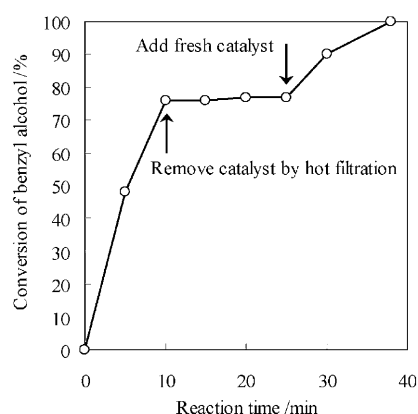
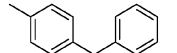
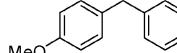
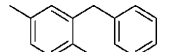
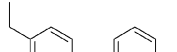
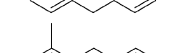
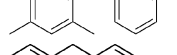
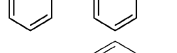
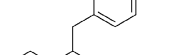
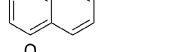


Figure 1. Catalyst separation at 10 min and triggering at 25 min.

finished in 5–10 min at a slightly higher temperature with 93–95% isolated yield. The benzylation of nonactivated arenes such as benzene (Table 2, entry 6, 94% yield) and naphthalene (Table 2, entry 7, 85% yield) proceeded smoothly. The more challenging reaction of the benzylation of acetophenone (Table 2, entry 8) gave the corresponding product in 15% yield with 88% selectivity for the *para* isomer. We noted that substituent effects greatly influenced the reactivity of arenes. For example, the reaction rate of benzyl alcohol with toluene was 12 times faster than that with acetophenone. Trifluoromethyl benzene, the least

Table 2. Reaction of benzyl alcohol with different arenes.^[a]

Entry	Arene	Major product	<i>T</i> [°C]	<i>t</i> [min]	Conv. [%]	Sel. [%]	YI [%] ^[b]	
1			2a	110	20	> 99	47:9:44 (<i>p:m:o</i>)	95
2			2b	110	20	> 99	51:49 (<i>p:o</i>)	94
3			2c	135	10	> 99	> 99	93
4			2d	135	5	> 99	46:12:42 (<i>p:m:o</i>)	93
5			2e	135	5	> 99	> 99	95
6			2f	80	90	> 99	> 99	94
7 ^[c]			2g	100	120	95	74:26 (<i>1:-2-</i>)	85
8			2h	110	60	25	88:12 (<i>p:o</i>)	15
9			2i	110	120	0	0	–

[a] Reaction condition, see Table 1, footnote a. [b] Yield of isolated product. [c] 0.78 mmol naphthalene, 26 μ L benzyl alcohol, 2.7 μ L hexadecane, 30 mg catalyst, heated to reflux in 2 mL 1,4-dioxane.

active species we studied (Table 2, entry 9), did not react with benzyl alcohol in a 120 min run.

Moreover, the MP catalyst could efficiently catalyze intramolecular benzylation (Table 3). The five-, six-, and seven-membered rings were formed by connecting two phenyl

Table 3. Intramolecular benzylation^[a]

Arene	Product	<i>t</i> [h]	Conv. [%] ^[b]	IY [%]
	3a	4	40	–
		10	97	88
	3b	4	> 99	92
	3c	4	42	–
		10	95	91

[a] Reaction conditions: substrate 2 mmol, solvent 1,4-dioxane 10 mL, catalyst 0.3 g, Ar protection, heated to reflux. [b] Determined by ¹H NMR spectroscopy.

rings. For instance, treatment of (2-benzylphenyl)methanol in 1,4-dioxane heated to reflux for 4 h produced 9,10-dihydroanthracene (**3b**) as the single product in 92 % yield. Similarly, a compound of 9H-fluorene (**3a**, yield 88 %) and 10,11-dihydro-5H-dibenzo[*a,d*]cycloheptene (**3c**, yield 91 %) were collected as mono products when employing biphenyl-2-ylmethanol and (2-phenethylphenyl)methanol as substrates, respectively. The reaction rate decreased in the sequence: **3b** > **3c** > **3a**, which could be explained by the increasing order of strain energies (kcal mol^{−1}): cyclohexane (−0.6) < cycloheptane (5.6) < cyclopentane (6.0).^[50]

We expected that the MP catalyst could also be applied to substituted benzylic alcohol as the alkylation agent. Catalytic reactions were carried out using *p*-xylene and various substituted benzyl alcohols (Table 4). As a result, electron-rich alcohols such as *p*- and *o*-methyl benzyl alcohol (Table 4, entries 2 and 3) afforded the corresponding benzylation of *p*-xylene in excellent yield (95 %). Even with bulky substituents at the benzylic carbon such as 1-phenylethanol (Table 4, entry 4) and diphenyl-

methanol (Table 4, entry 5), quantitative yields of benzylation of arenes were obtained. The benzylation with electron-poor alcohols also proceeded smoothly by increasing reaction time and temperature (Table 4, entries 6 and 7). More interestingly, the reaction of chlorobenzyl alcohol with *p*-xylene resulted in a spectacular yield (93 %). It is worthy noting that the latter reaction is one of the few successful Friedel–Crafts benzylation reactions that worked well with deactivated arenes. However, for the *p*-CF₃-substituted benzyl alcohol (Table 4, entry 8), the reaction did not take place under these conditions.

Kinetic runs were carried out in the benzylation of toluene at temperatures ranging from 90 to 110 °C. The initial concentration of benzyl alcohol was 0.15 mol L^{−1}. The reaction pressure was kept constant at 1 atm. The stirring speed was over 500 rotations per minute (RPM) to eliminate mass transfer limitations. The concentration of toluene is considered to be constant. Thus, the rate equation is simplified as: $-d[\text{alcohol}] = k[\text{cat}][\text{alcohol}]dt = k_{\text{obs}}[\text{alcohol}]dt$. The k_{obs} values at 363, 373, and 383 K are based on data from Figure 2a and are calculated to be 8.4×10^{-5} , 1.4×10^{-4} , and 4.8×10^{-4} mol^{−1} L^{−1} s^{−1}, respectively. From the Arrhenius plot of $\ln k_{\text{obs}}$ versus $1/T$ shown in Figure 2b, the activation energy E_a is evaluated to be 96.1 kJ mol^{−1} using the first-order fit, which is smaller than the value of 106 kJ mol^{−1} obtained for the reaction on Nafion-silica composite.^[51]

Material synthesis and general characterization: The catalyst precursor precipitated from a solution mixture of acetone

Table 4. Reaction of *p*-xylene with different alcohols.^[a]

Entry	Alcohol substrate	Product	<i>T</i> [°C]	<i>t</i> [min]	Conv. [%]	Sel. [%]	IY [%]
1		4a	135	10	> 99	> 99 ^[b]	93
2		4b	110	15	> 99	> 99 ^[b]	95
3		4c	110	20	> 99	> 99 ^[b]	95
4		4d	110	45	> 99	> 99 ^[b]	96
5		4e	110	60	98 ^[c]	> 99 ^[c]	88
6		4f	130	180	> 99 ^[c]	> 99 ^[c]	90
7		4g	130	180	> 99 ^[c]	> 99 ^[c]	93
8		4h	130	180	0 ^[c]	–	–

[a] Reaction conditions, see Table 1 footnote a. [b] Determined by GC. [c] Determined by ¹H NMR spectroscopy.

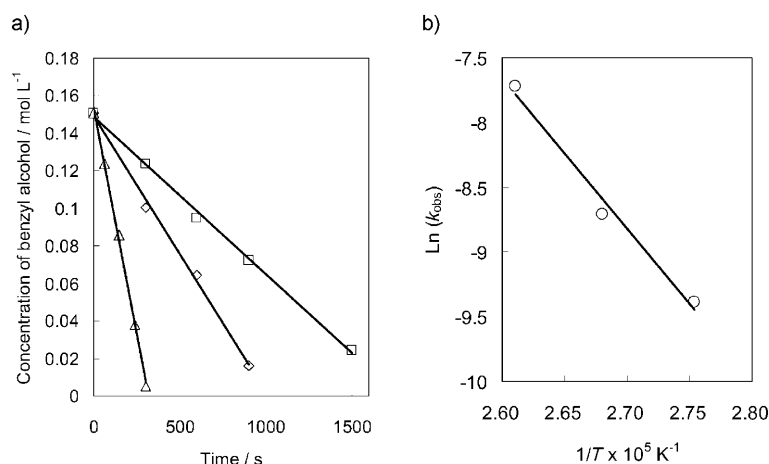


Figure 2. a) The kinetic analysis of the benzylation of toluene over the MP catalyst. b) Arrhenius plot.

and water has the vibration frequencies at 917, 892, 841, 652, 577, and 478 cm^{-1} (see Figure S2 in the Supporting Information). According to the literature,^[52] these bands correspond to the $\text{Mo}_7\text{O}_{24}^{6-}$ species. The isopolymolybdate structure of the heptamolybdate salt was not affected during the precipitation process since the IR bands in the range of 1000–400 cm^{-1} are very sensitive to a small change in the cluster structure.^[52] Furthermore, there are no products from acetone, as monitored by using mass spectrometry. Molybdates in aqueous solution form a vast variety of structures due to the flexibility in the Mo–O–Mo link. In this research, acetone was used to decrease the outer polarity of the macroanion molybdate clusters, which are highly hydrated and interconnected by weak hydrogen bonds as proposed by Müller et al.^[53] The interaction balance is disrupted by acetone, and, therefore, the small clusters with acetone and water periphery are driven to precipitation. As discussed previously, the direct calcination of the molybdate salt $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (AHM) does not afford a highly active catalyst. Thus, we reason that the small clusters are necessary to obtain the nanostructured and active catalyst. Acetone is the best solvent for this purpose. We did not obtain any precipitate by replacing acetone (dielectric constant $\epsilon=21$) with glycerol ($\epsilon=46$), acetonitrile ($\epsilon=37$), methanol ($\epsilon=33$), ethanol ($\epsilon=24$), benzyl 2-butanone ($\epsilon=19$), benzyl alcohol ($\epsilon=12$), and chloroform ($\epsilon=10$). This may be due to the fact that the interaction of acetone with water is unique and of medium strength. Solvents with larger ϵ are miscible with water and the ones with smaller ϵ are immiscible with water.

The calcination of molybdate salt (MM), the commercial MoO_3 (MC- MoO_3), and the MP are orthorhombic crystals, exhibiting the typical (020), (110), (021), and (111) of α -phase MoO_3 (JCPDS 05–0508) (Figure 3). The calcination of the catalyst precursor under a N_2 atmosphere affords MP-NC with a reduced phase (monoclinic phase Mo_4O_{11} , JCPDS 65–2473). The orthorhombic phase MoO_3 is a layered structure stacked parallel to the (010) plane, in which each layer is composed of bilayers of Mo–O octahedrons.

The ratio of (040) to (021) of MP is 0.24, which is much smaller than the 1.62 of MC- MoO_3 , suggesting that the anisotropic growth of MP is decreased and forms a thin pellet structure.

Table 1 lists several properties of these oxides. The colors of the samples are different. The deep blue color of MP-NC relative to the light blue color of MP reflects a phase reduction during calcination under a N_2 atmosphere. Both MC- MoO_3 and MM have a small surface area. After milling MM

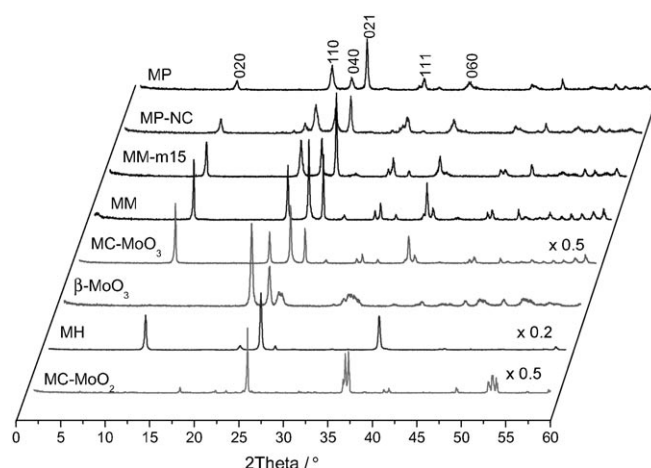


Figure 3. The X-ray diffraction patterns of various molybdenum oxides. The intensities of MC- MoO_3 , MH, and MC- MoO_2 were multiplied by the number on the right to give a reasonable scale.

for 15 min, the surface area increased to 20.5 $\text{m}^2 \text{g}^{-1}$. The increase in surface area could explain the higher activity of MM-m15 and the lower selectivity of alkylated product (Table 1).^[54] The MP-NC has a larger surface area than MP due to shear reduction.^[55] The crystallite sizes are calculated by Sherrer's formula ($D_{hkl}=0.9\lambda/[\beta\cos\theta]$) on three diffraction peaks of (020), (110), and (021). The size of the (110) and (020) facets of MP are 26% and 43% of that of MC- MoO_3 , respectively. The milling process decreased the crystallite size, as evidenced by comparing MM-m15 (MM after milling for 15 min) and MM. The surface morphology was observed by using electron microscopy (see Figure S3 in the Supporting Information). MC- MoO_3 , MM, and MP have pellet structures with an exposed (010) basal plane. However, the thickness of MP is about 30 nm (Figure 4), which is consistent with the X-ray diffraction data. The lateral length of MP lies within a narrow distribution of 400–500 nm. The MC- MoO_3 is microscale with a broad distribution centering at between 1.0 and 1.5 μm . (Figure 5).

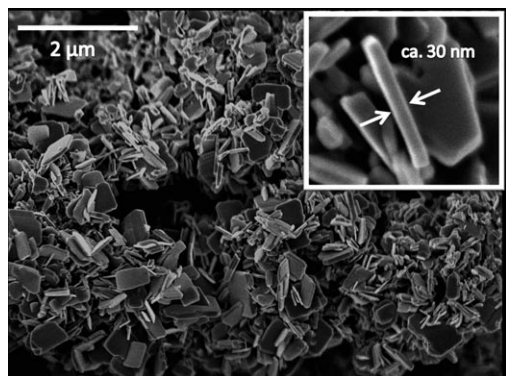


Figure 4. Representative SEM image of the MP catalyst. Inset image shows the thickness of the pellet.

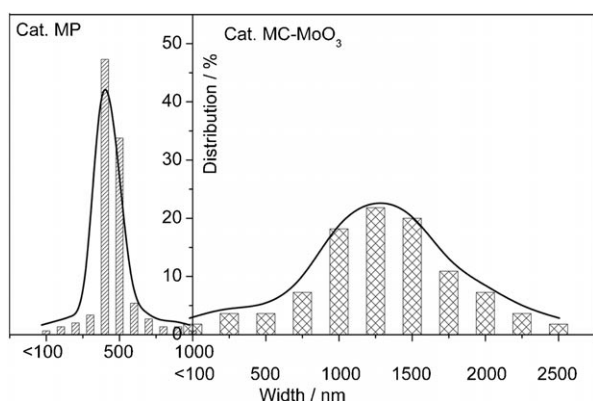


Figure 5. The histogram of the lateral length distribution. About 200 particles were counted along the x and y directions of the SEM images to give the statistical result.

Thermogravimetric analysis (TGA) of the precipitate and the catalyst precursor were performed in air. The plot of the weight loss against temperature is given in Figure 6, which shows three distinctive peaks at 122, 305, and about 400 °C, and one shoulder at 235 °C. On the basis of the temperature-programmed desorption mass spectrometric (TPD-MS) profile (Figure 7), no acetone is detected. The peak at about 122 °C corresponds to weakly adsorbed water, as represented by the mass-charge ratio (m/z) of 18. The peak at 235 °C

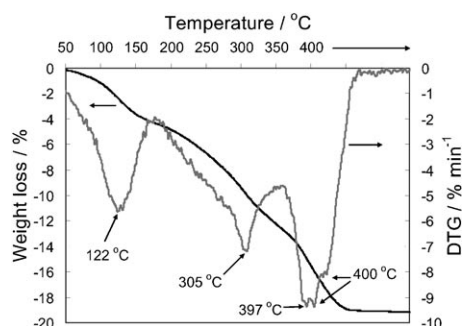


Figure 6. The TGA and DTG profiles of the precursor of the MP catalyst. Carrier gas was air. The temperature was kept at 400 °C until no obvious weight loss was observed.

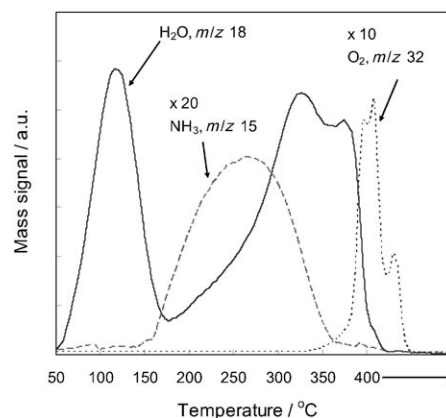


Figure 7. Temperature-programmed decomposition in helium, and mass spectrometry (TPD-MS) profile of the MP precursor.

is due to NH_3 , as monitored by m/z 15. The generation of NH_3 is accompanied by the release of water, as illustrated by the similar onset temperature of water at about 170 °C. We note that the release temperature of NH_3 is much lower than the 310 °C of calcining $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (AHM), suggesting that NH_3 was bonded more weakly in the catalyst precursor than in AHM. The peak at 305 °C is attributed to water. Notably, m/z 32, representative of oxygen, is evolved at about 400 °C. We did not observe the oxygen release during calcining the AHM salt.

The composition of the precipitate precursor was estimated by assuming that the composition at 330 °C (before releasing oxygen) is equivalent to MoO_3 . A general formula of $((\text{NH}_4)_2\text{O})_x \cdot \text{MoO}_3 \cdot (\text{H}_2\text{O})_y$ proposed by Zeng et al. was employed.^[3] The weight loss at 330 °C is 13.1 %, which can be ascribed to the combined loss of adsorbed water (4.3 %) and both NH_3 and dehydrated water (8.8 %). The calculated values of x and y are 0.169 and 0.239, respectively. Thus, the precursor formula can be expressed as $((\text{NH}_4)_2\text{O})_{0.169} \cdot \text{MoO}_3 \cdot (\text{H}_2\text{O})_{0.239}$. Compared to the hydrothermally prepared precursor of $((\text{NH}_4)_2\text{O})_{0.0866} \cdot \text{MoO}_3 \cdot (\text{H}_2\text{O})_{0.231}$,^[3] the precipitate precursor contains more interlinked NH_3 and water, which tends to create a larger interval space and generate edges after releasing NH_3 and water in calcination, as illustrated by the card-house morphology of the MP catalyst (see Figure 4).

For the MP catalyst, the release of oxygen at about 400 °C in air is a sign of weakly held oxygen species. We reason that the surface molybdenum octahedron is severely distorted on the nanostructured MoO_3 . As a result, the strength of the $\text{Mo}=\text{O}$ bond on the (010) facet is weakened (see below), and the oxygen becomes more active compared with an ideal MoO_3 surface.^[55] Both TGA and TPD-MS showed three peaks at 400 °C, suggesting terminal, bridging, and three-coordinate oxygen atoms, which agrees well with the literature.^[15]

The catalytic activities and product selectivities are greatly dependent on the calcination temperature of the MP precursor (Figure 8). The catalyst exhibits low activity from 250 °C, reaches a maximum of $19.2 \mu\text{mol min}^{-1} \text{g}^{-1}$ at 330 °C,

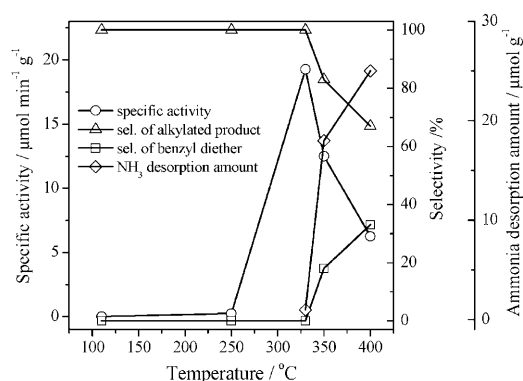


Figure 8. The changes in specific activity, product selectivity, and catalyst acidity as a function of calcination temperature.

and decreases to $6.25 \mu\text{mol min}^{-1} \text{g}^{-1}$ at 400°C . Prior to reaching the temperature of 330°C , the product is mono-alkylated toluene. The byproduct of benzyl diether is produced at 350°C , and reached 33% at 400°C .

Ammonia molecules interact with Lewis (L) acid sites through N-metal bonding and with Brønsted (B) sites through N-H-O bonding on the oxide surface.^[56,57] Normally, bulk MoO_3 has an acidity of $20 \mu\text{mol g}^{-1}$.^[46] However, as shown in Figure 8, in addition to its high specific surface area, the MP has no acidity (about $0 \mu\text{mol g}^{-1}$). Compared to the acidity of MM of $12 \mu\text{mol g}^{-1}$, it is obvious that the surface of nanostructured MoO_3 is very different from the surface of bulk MoO_3 . This also means that the nanostructured MoO_3 contains fully oxygen-coordinated MoO_6 octahedrons on the surface, and the benzylation reaction on the nanostructured MoO_3 is not of an acid-catalyzed type. Under the calcination temperatures of 350 and 400°C , according to the results of the TPD-MS, the oxygen vacancies are created, and correspondingly, the acidity is increased, and reaches $25 \mu\text{mol g}^{-1}$ at 400°C . Simultaneously, the selectivity to BDE is increased because the reaction is catalyzed by acid sites.^[49]

Combining the results of catalytic tests, TGA, TPD-MS, and the TPD of ammonia (NH_3 -TPD), we came to the following conclusions: 1) the decomposition of the catalyst precursor to NH_3 and H_2O at 235°C does not generate active sites; 2) the active sites are created at 330°C after elimination of NH_3 and water; 3) the active sites are lost after releasing oxygen, which leads to acid sites; 4) the selective and active sites on the MP catalyst toward the alkylated product are non-acidic, and the acidic sites produce byproducts.

The anisotropic growth of the MoO_3 crystal forms a pellet morphology with the most exposed facet as (010).^[15] There have been many disputes concerning the active facet of MoO_3 in selective oxidation.^[27,28] However, in benzylation, we conclude that the active facet of the nanostructured MoO_3 is the basal (010) facet. The edge facets, such as (100) and (001), are nonselective sites for benzylation. This conclusion is based on milling tests and comparison with the MH catalyst. As shown in Table 5, the mechanical activation

Table 5. Control experiment of the MP catalysts and comparison with MH catalyst.^[a]

Cat	Facet ratio ^[b]		Acidity ^[c] [$\mu\text{mol g}^{-1}$]	S [$\text{m}^2 \text{g}^{-1}$]	Conv. [%]	Sel. [%] ^[d]	
	010	non-010				AP	BDE
MP	88	12	ca. 0	14.6	76	100	0
milled MP ^[e]	67	33	11	23.5	82	83	17
MH	1	99	4	7.7	28	97	3

[a] Reaction conditions: alcohol 0.24 mL, arene 15.0 mL, hexadecane (internal standard) 0.1 mL, reaction temperature 110°C , catalyst 0.3 g, sampling time 10 min, Ar protection. [b] The facet ratio was estimated by counting about 100 particles in SEM images. [c] The amount of ammonia desorption. [d] AP: alkylated product; BDE: benzyl diether. [e] The MP was manually milled for 10 min in a mortar.

of the MP catalyst by ball milling increases the ratio of non-facet (010) from 12 to 33%. As a result, the milled MP has an acidity of $11 \mu\text{mol g}^{-1}$, suggesting that acidic sites are created on side facets by milling. The MH is a catalyst anisotropically grown along the [010] direction to form a cuboid structure $3 \mu\text{m}$ long and 100 nm thick. The ratio of the (010) facet of MH is about 1%. Catalytic results show the milling process increases the conversion from 76 to 82%, due to the increased surface area. However, the milling process leads to a decrease in the selectivity for the alkylated product. About 17% of benzyl diether (BDE) is produced as a byproduct. These results are understandable since the milling process breaks the Mo-O-Mo bonds on the edge facets, and creates acidic sites, which catalyze the formation of BDE.^[54] In comparison, MH is much less active than MP. This also suggests that the benzylation takes place on a (010) facet.

The technique of electron spin resonance (ESR) is very sensitive to the electronic structure and the symmetry of the surroundings of paramagnetic species.^[58] Stoichiometric MoO_3 containing Mo^{6+} has no 4d electrons and is a diamagnetic insulator. A disturbance in its stoichiometry by the formation of oxygen vacancies causes the generation of $4d^1$ (Mo^{5+} , $S=1/2$), which is expected to give an ESR signal. The ESR spectrum of MM is found to be featureless (Figure 9), indicating that the valence of molybdenum is 6+. The MP-250 exhibits a detectable signal at $g=1.956$, show-

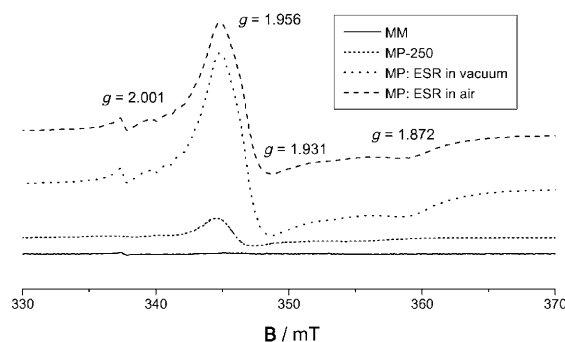


Figure 9. The ESR spectra of MM, MP-250, and MP in a vacuum and MP in air.

ing the start of the formation of a Mo^{5+} center. For MP in a vacuum, the signals appear at g values of 2.001, 1.956, 1.931, and 1.872. The later g values, which are the most intense signals, are comparable to those reported for MoO_3 single crystals and are characterized as Mo^{5+} ions in an orthorhombic distorted, sixfold coordination.^[54] The distinctive asymmetry of these signals indicates severely distorted Mo^{5+} centers. The appearance of the signal at $g=2.001$ is indicative of unpaired electrons, which are the reason for the blue color of the MP catalyst. The unpaired electrons may be confined to oxygen defects, which are located between two molybdenum metal sites within the bulk phase, similar to F-type defect centers.^[59] Some other examples of blue materials with confined electrons in defects or three-dimensional pores are nanocrystalline MgO ,^[60] zeolites,^[61] or inorganic electrides.^[62] The signal at $g=2.001$ did not disappear after exposing the MP to air, which is evidence that the unpaired electrons are located within the bulk phase.^[63]

The X-ray photoelectron spectroscopy (XPS) spectra recorded on MM and MP are given in Figure 10. The doublets in the binding energies reflect the Mo oxidation states pres-

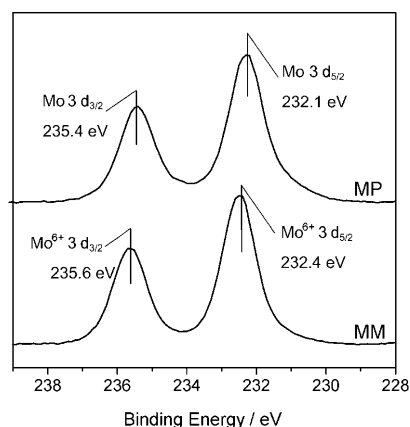


Figure 10. The XPS spectra of Mo $3d_{3/2}$ and Mo $3d_{5/2}$ of the MM and MP catalysts.

ent in these catalysts. The doublets in the binding energies at 235.6 and 232.4 eV for MM are attributed, respectively, to the binding energies of the $3d_{3/2}$ and $3d_{5/2}$ electrons of Mo^{6+} . The integral areas between the two doublets are in a ratio of 2:3, and the energy gap between them is 3.2 eV, in agreement with standard data.^[64] In comparison to the MM catalyst, the two peaks of the MP catalyst are shifted slightly lower in energy (235.4 and 232.1 eV for $3d_{3/2}$ and $3d_{5/2}$, respectively), which is indicative of an extra electron around the Mo^{6+} center, but not a complete reduction to Mo^{5+} . It is known that an extra electron can lower the inner electron binding energy of the core metallic cations. Therefore, we infer that for the MP catalyst, the electron from Mo^{5+} relative to Mo^{6+} is actually delocalized to a great degree, and not bound tightly to an individual Mo^{6+} core cation. In this regard, it is reasonable that only one set of doublets is de-

tected, which slightly decreases the corresponding binding energies due to delocalized electrons.

The ultraviolet-visible (UV/Vis) spectra of MM, MP, and MP-NC are given in Figure 11. The absorption edge energy (AE) provides an accurate description of the electronic

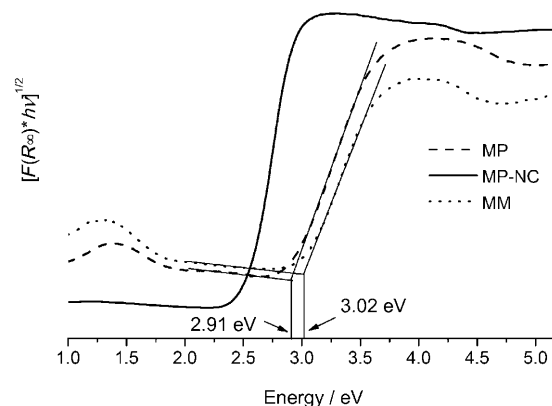
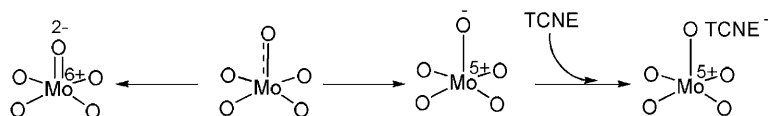


Figure 11. Diffuse reflectance UV/Vis spectra of MM, MP, and MP-NC. All spectra use the Kubelka–Munk formalism and assume indirect ligand to metal charge transfer (LMCT) transitions. Edge energies (AE) are defined by convention as the x intercept of a linearized near-edge region for $[F(R8)*hv]^{1/2}$ as a function of $h\nu$, where $F(R8)$ is the Kubelka–Munk function and $h\nu$ is the energy of the incident photon.

properties of metal oxides because it corresponds to the energy needed for electron transfer from the oxygen of an oxide to the metal site.^[65,66] The MM catalyst has an AE value close to that of common bulk MoO_3 .^[65,67] The blue MP catalyst is darker than the light gray hue of MM. This is quantitatively measured by a 0.11 eV smaller AE value than that of MM. This suggests that the energy required to promote an electron from the highest occupied molecular orbital (HOMO) in an oxygen atom to the lowest unoccupied molecular orbital (LUMO) in the Mo cation of MP decreases. Correspondingly, for the MP catalyst, the backdonation from an oxygen atom to a Mo atom becomes possible. These results are also consistent with similar trends observed for dispersed MoO_x .^[65,68] The absorption peak at 1.3 eV of MM can be ascribed to intervalence charge transfer (IVCT) transitions of Mo^{6+} -O- Mo^{5+} . The blue shift to 1.4 eV and broadened band absorption of MP is a diagnostic of diminution of particle size as well as the strain in the oxide lattice induced by severely distorted MoO_6 octahedrons.^[13] This phenomenon was previously observed on a nanocomposite material.^[69,70] No absorption band for IVCT was observed on MP-NC, suggesting the entire reduction of the sample.

During our experiments, we observed that the light blue MP catalyst changed to dark blue. Based on this, we infer that some electrons may be delocalized to a Mo^{6+} site during activation of the benzyl alcohol. As a result, the nature of the Mo=O bond will be partially ionic if electrons hop between metal centers and oxygen atoms on the MP surface.^[16] In an extreme state, in which one electron is en-

tirely back donated to a Mo^{6+} site, one unpaired electron will be located around an oxygen atom (Scheme 1). As a result, the terminal oxygen atom may have the ability to



Scheme 1. The surface electron transfer from a terminal oxygen atom to a Mo atom or to an electron acceptor (TCNE, tetracyanoethylene).

donate the unpaired electron or to accept one extra electron from an external source to form a stable bond. In our research, we employed an electron acceptor to probe the unpaired electron. Tetracyanoethylene (TCNE) is a common electron acceptor with an electron affinity value of 2.3. The appearance of a blue anion radical of TCNE^{-•}, an electron-transfer complex detectable by UV/Vis spectrometry at about 330 nm,^[71,72] is the evidence of such a reaction and is given in Scheme 1.

The adsorption test of TCNE on the MP catalyst was conducted at 80 °C in acetonitrile. The reaction reached equilibrium in 10 min as judged by UV/Vis spectroscopy. The color of the catalyst changed to dark blue. The UV/Vis spectra of a fresh TCNE acetonitrile solution and the reacted solution are given in Figure 12. A distinctive adsorption peak shows

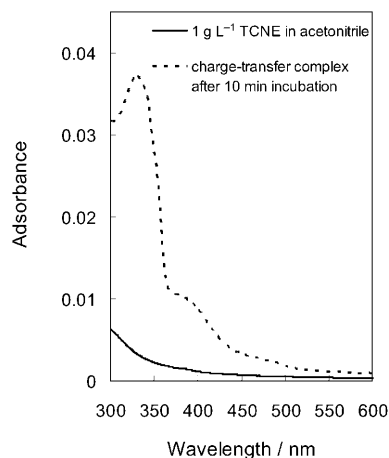


Figure 12. The UV/Vis spectra of fresh TCNE (tetracyanoethylene) acetonitrile solution (solid line) and charge-transfer complex of TCNE^{-•} (dashed line).

up at 328 nm, which is the evidence of the formation of the charge-transfer complex TCNE^{-•}. We note that this is the first time the electron donation ability of nanostructured pure MoO_3 was observed. Using the molar adsorption value of $3800 \text{ mol L}^{-1} \text{ cm}^{-1}$ for TCNE^{-•},^[73] the concentration was calculated to be $6 \times 10^{-8} \text{ mol L}^{-1}$. Given that one anion radical corresponds to one terminal $\text{Mo}=\text{O}$ site in Scheme 1, the density of $\text{Mo}=\text{O}$ sites per surface area of the catalyst is estimated to be $4 \times 10^{15} \text{ unit cm}^{-2}$. Assuming that the radius of one octahedron is $1.8 \text{ \AA}$, the surface terminal $\text{Mo}=\text{O}$ bond is

close to $1 \times 10^{16} \text{ unit cm}^{-2}$. The two values are approximate, suggesting that the adsorption site is terminal $\text{Mo}=\text{O}$. The difference between the two values may be due to steric effects since some $\text{Mo}=\text{O}$ sites, such as those located in reverse corners and steps, cannot be reached by TCNE.

It would be of great interest to know the effect of various electron acceptors with different electron affinity on the catalytic performance of the MP in benzylation. A series of electron donors are listed in Table S1 in the Supporting Information. The dependence of specific activity on the electron affinity is shown in Figure 13. The addition of nitrobenzene (electron affinity: 1.0 eV) has no effect on the catalytic activity. The decrease of catalytic activity starts with the addition of *m*-bromonitrobenzene (1.3 eV) and becomes apparent by adding *o*-dinitrobenzene (1.6 eV). With the large electron affinity of TCNE (2.3 eV), the decrease reaches 85% of the original catalytic activity. Although the electron affinity of tetracyano-*p*-quinodimethane (TCNQ, 2.8 eV) is larger than that of TCNE, it has almost no influence on the catalytic activity (Figure 13). In this case, the steric effect has to be considered because adsorption sites are located on flat surfaces or in corners. In comparison, these electron acceptors have no effect on the performances of the MM catalyst (Figure 13), suggesting that the reaction on the bulk MoO_3 is not catalyzed by terminal oxygen sites.

We conclude the following points from these tests: 1) the terminal oxygen of the nanostructured MoO_3 catalyst, which can be molecularly probed with electron acceptors, is very different from that of bulk MoO_3 surfaces; and 2) the terminal oxygen of the nanostructured MoO_3 is the active site for electron transfer and also for benzyl alcohol activation.

The MoO_3 (010) surface contains three types of oxygen centers (Figure 14, inset geometric structure): one unshared

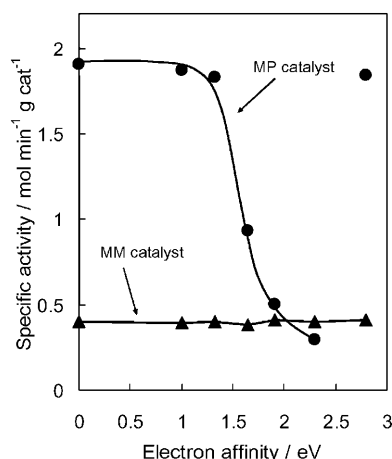


Figure 13. The effect of various electron acceptors with different electron affinity on the catalytic activity of the MP and MM catalyst in the benzylation of toluene with benzyl alcohol.

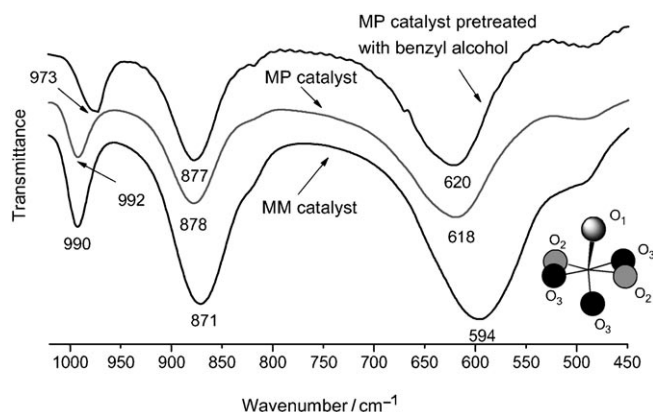


Figure 14. IR spectra of MM, MP, and the benzyl alcohol adsorbed MP catalyst. The scheme in the inset shows the geometric structure of oxygen coordinated Mo octahedron.

terminal oxygen atom O_1 located in the (010) plane, two axial oxygen atoms O_2 located asymmetrically between two Mo centers, and three equatorial oxygen atoms O_3 located symmetrically between two Mo centers and linking another Mo center. The IR spectra of MM, MP, and pretreated MP catalyst are given in Figure 14. Three main adsorption peaks and their changes with samples are observed. The MM shows characteristic IR patterns similar to those of bulk MoO_3 .^[54,74] A very sharp band at 990 cm^{-1} is due to the $\nu\text{Mo}=\text{O}_1$ stretching vibration. The second intense band at 871 cm^{-1} is assigned to the $\text{Mo}-\text{O}_2-\text{Mo}$ vibration. The third broad peak at 594 cm^{-1} is ascribed to the vibration of $\text{O}_3-\text{Mo}-\text{O}_3'$. For the MP spectrum, these three bands shift to 992, 877, and 618 cm^{-1} , respectively. Such phenomena are known for nanocomposite materials and are the evidence of quantum confinement due to particle size.^[75–77] The adsorption of benzyl alcohol on the MP catalyst leads to an apparent shift of the peak at 992 cm^{-1} to 973 cm^{-1} and slightly affects the other two peaks at 877 cm^{-1} and 620 cm^{-1} . It was reported that the introduction of an extra electron into oxides, such as pure V_2O_5 , could cause a redshift in the stretching band of the $\text{V}=\text{O}$ group^[48] due to the relaxation of surface energy.^[78] Therefore, the most affected stretching band of the terminal $\text{Mo}=\text{O}$ strongly proves that the adsorbed benzyl alcohol transfers an electron to a $\text{Mo}=\text{O}$ site. As a result, benzyl alcohol is activated on a $\text{Mo}=\text{O}$ site and forms a benzyl carbocation. One electron from an oxygen atom is lent to a Mo^{6+} site, and, thus, the charge of Mo is lower than $6+$, close to $5+$, which is the reason for the color change of the catalyst to dark blue.

The catalyst structure and reaction mechanism is given in Figure 15. The $\alpha\text{-MoO}_3$ contains a slab of two layers of edge-shared Mo octahedrons. The slab, equal to one and half octahedra, has a height of about $6\text{ \AA}$. One pellet of about 30 nm consists of roughly 50 slabs, which are connected along the [010] direction by van der Waals forces. Oxygen vacancies are located within the bulk phase. Free electrons are stabilized within the oxygen vacancies, similar to electrides.^[62] The surface layers of (010) facets contain

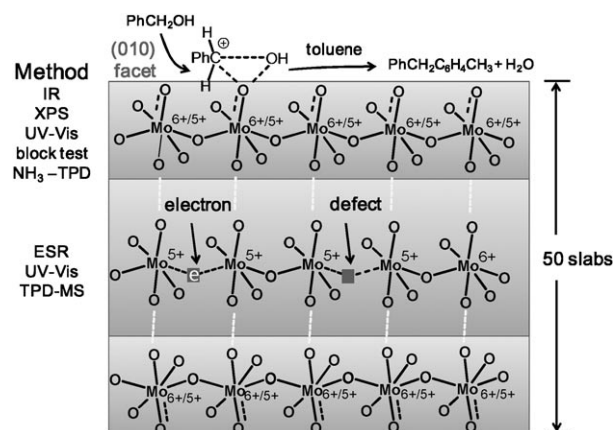


Figure 15. The understanding of the nanostructured MoO_3 by various characterization techniques, and reaction mechanism in the benzylation of toluene with benzyl alcohol.

fully oxygen-coordinated Mo sites. The whole material can be pictured as distorted octahedron layers supported on partially reduced MoO_3 . The catalytic reactions take place on the (010) facets. The oxygen atoms of terminal $\text{Mo}=\text{O}$ sites, which resemble oxygen anion radicals, adsorb and activate benzyl alcohol by electrophilic attack. Due to the high density and uniform distribution of $\text{Mo}=\text{O}$ sites on the (010) facet, the nanostructured MoO_3 shows excellent activity and selectivity. The dissociation of the PhCH_2-OH (Ph = phenyl) bond forms a benzyl carbocation, which is further reacts with toluene to form the product and water, the desorption of which from the catalyst surface recovers the active sites so that they are ready for the next catalytic cycle. The absence of any oxidized product and the high reusability suggests that the surface $\text{Mo}=\text{O}$ is not broken during the reaction, otherwise the catalyst would soon lose activity.

Conclusion

In summary, we have demonstrated that nanostructured MoO_3 is a highly active and selective catalyst for the alkylation reaction. The method was extended to synthesize diphenylmethane derivatives from various substituted benzyl alcohols and substituted arenes. The ability to selectively activate the $\text{C}-\text{X}$ ($\text{X}=\text{OH}$, Cl) bond shows its potential application to other catalytic reactions, such as selective oxidation and dechlorination. The catalyst preparation is facile and does not require hydrothermal processes and organic templates. Catalyst characterization results suggest that the nanostructured MoO_3 platelet with a thickness about 30 nm contains active $\text{Mo}=\text{O}$ bonds on the (010) facet. The active facet for the benzylation is the (010) facet. The terminal oxygen atom has radical properties and is very active towards the adsorption and activation of benzyl alcohol. The reactions catalyzed by bulk MoO_3 (MM and MC- MoO_3) with normal surface $\text{Mo}=\text{O}$ bonds, or by a reduced nanostructured MoO_3 (MP-NC) are sluggish and less selective.

The present work will be helpful in understanding heterogeneous catalysis on the surface of nanomaterials.

Experimental Section

All chemicals were purchased from Wako Pure Chemical Industries. These chemicals were used without further purification. All reagents were A.R. grade. Distilled water was prepared by using Yamato Autostill WG25 (Tokyo, Japan).

Preparation of MP: In a 2 L beaker, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (AHM; 15 g) was added to water (500 mL). The solution was stirred for 5 min at room temperature until a clear solution had formed. One liter of acetone was poured into the solution to cause precipitation. The mixture was aged for 7 min, and then the solid was filtered off. The filtrate was washed with acetone (2×100 mL) and pentane (2×20 mL), and then dried at 60°C in an oven for 14 h. The precipitate was calcined at 330°C for 2 h with a ramp of $10^\circ\text{C min}^{-1}$ in air. The sample was designated as MP. The samples calcined at 250, 350, and 400°C were designated as MP-250, MP-350, and MP-400, respectively. The sample calcined in a N_2 flow (50 mL min^{-1}) was designated as MP-NC.

Preparation of MM: AHM (2 g) was spread as a thin layer in a crucible and calcined in an oven at 500°C for 12 h. The sample was designated as MM. The MM-m15 sample was prepared by milling MM for 15 min at 150 RPM. The procedures for preparing $\text{MH}^{[79]}$ and $\beta\text{-MoO}_3^{[80]}$ are detailed in the Supporting Information. MC-MoO_3 and MC-MoO_2 were commercial products (Wako Chemicals).

Catalysis: A 50 mL round-bottom three-neck flask equipped with a reflux condenser was used as a stirred bed reactor to test the catalytic activities. Typically, 0.3 g of catalyst and a Teflon coated magnetic stir bar were loaded into the reactor. The reactor was sealed and purged with N_2 (10 mL min^{-1}) under the desired temperature for 5 min. The oil bath was removed and the reactor was cooled to ambient temperatures. A mixture of benzyl alcohol (0.24 mL), arenes (15 mL), and an internal standard, hexadecane (0.1 mL), were added to the reactor. The mixture was purged with N_2 (10 mL min^{-1}) for 3 min. The reactor was then placed in the oil bath. The mixture was stirred until the reaction reached completion, as judged by TLC. Aliquots (0.1 mL) were collected at intervals. The concentrations of reactant and product were measured by gas chromatography using a flame ionization detector (Shimadzu Classic-5000, 60 m TC WAX column), operated with a heating program: 120°C for 10 min, ramp $10^\circ\text{C min}^{-1}$ to 250°C (kept for 20 min). The crude mixture was concentrated in vacuo to yield the crude product. Purification of the product was carried out on silica gel using pure hexane to remove the remaining solvent, followed by washing with hexane/ethyl acetate (2.5:1) to give the desired diphenylmethane compound. $^1\text{H NMR}$ and $^{13}\text{C NMR}$ spectra were recorded by using a JEOL ECX-600 or a JEOL ECX-400 at the CRIS center of Hokkaido University. The $^1\text{H NMR}$ and $^{13}\text{C NMR}$ spectra were conducted in CDCl_3 under ambient conditions with TMS as the standard (1 wt% in CDCl_3) or with CHCl_3 as reference ($\delta = 7.26$ ppm). The spectra of known compounds (Table 2 and Table 4) were identical to those reported in the literature, and unavailable spectra and the spectra of new compounds (Table 4, entry 2–7) are appended as Supporting Information.

General characterization: Powder X-ray diffraction (XRD) measurements were performed with a Rigaku, RINT Ultima+ diffractometer with $\text{Cu K}\alpha$ radiation ($K\alpha$ 1.54056 Å) and X-ray power of 40 kV/20 mA. The crystallite size was calculated from the line broadening using the Scherrer formula. Shirley background correction procedures and least-squares fittings methods were adopted for data processing. Field-emission scanning electron microscopy (FE-SEM) was performed on a JSM-7400F (JEOL). Samples for SEM were dusted on an adhesive conductive carbon paper attached on a brass mount. Specific surface areas were measured by N_2 adsorption at 77 K using the Brunauer–Emmett–Teller method (BET)^[81] over Autosorb 6 AG (Quantachrome Instruments).

The electron spin resonance (ESR) spectra at X band (9 GHz) were measured by using a JEOL RE-2X spectrometer. The magnetic field was

swept from 100 to 13000 G. The g values were calculated by using the formula $h\nu = g\mu_B B$, where h is the Planck constant ($6.6261\times 10^{-34}\text{ J s}$), ν is the microwave frequency (9.438 GHz), μ_B is the Bohr magneton ($9.274\times 10^{-24}\text{ J T}^{-1}$) and B is magnetic field strength measured in tesla (T). The XP spectrum (XPS) was obtained by using a JPC-9010MC. A monochromated $\text{Mg K}\alpha$ (10 kV; 10 mA) line was used as X-ray source. The pressure in the analyzing chamber was 1×10^{-6} Torr during measurement. Binding energies of peaks were corrected by referencing the C 1s signal of adventitious contamination hydrocarbon to 284.2 eV.

The UV/Vis spectra were collected on a spectrophotometer (V-570, JASCO). For solid samples, the reference sample was BaSO_4 . The procedures employed for the tetracyanoethylene (TCNE) adsorption were the following. Acetonitrile (HPLC grade) was dried over 4 Å molecular sieves overnight and degassed with Ar for 2 min prior to use. The tetracyanoethylene (TCNE) solution (1 mg mL^{-1}) was prepared in a 10 mL volumetric flask. The fresh catalyst and magnetic stir bar were placed in a 25 mL flask and pretreated under N_2 flow at 80°C for 10 min, followed by addition of TCNE solution (8 mL). The reaction reached equilibrium after 10 min. The spectra of the solutions were measured. IR spectra were recorded on a Perkin Elmer FTIR spectrometer. The sample pellet with a 1.5 mm diameter was prepared by pressing a mixture of sample and KBr. The IR spectra were recorded by accumulating 32 scans at a spectra resolution of 2 cm^{-1} .

The measurements of thermogravimetric-differential thermal analysis (TG-DTA) were performed on a TG-8120 (Rigaku) thermogravimetric analyzer. Dry air or N_2 provided by a pressure tank with a flow rate of 30 mL min^{-1} was used as the carrier gas. The catalyst sample and standard were loaded into two alumina pans and heated at $10^\circ\text{C min}^{-1}$ to the desired temperature. The baseline was subtracted from a blank run without loading the sample.

Temperature-programmed desorption (TPD) of ammonia, NH_3 -TPD, was employed to measure oxide surface basicity. The experiment was carried out on a BELSORP apparatus. The experimental procedure was as follows. The catalyst (ca. 80 mg) was set up between two layers of quartz wool and pre-heated under helium (50 mL min^{-1}) at 300°C for 1 h. Then, ammonia was introduced at 100°C for 30 min. The desorption profile was recorded with a mass spectrometer from 100°C to 600°C under helium flow (50 mL min^{-1}). Temperature-programmed decomposition mass spectrometry (TPD-MS) measurements were performed from 120 to 600°C at a heating rate of $10^\circ\text{C min}^{-1}$ in helium flow (50 mL min^{-1}). The decomposed gas molecules were monitored by a mass spectrometer (ANELVA, Quadrupole Mass Spectrometer, M-100QA, BEL Japan), collecting several mass fragments: acetone (m/z 58), NO_2 (46), CO_2 (44), O_2 (32), NO (30), N_2 (28), H_2O (18, 17, 16), NH_3 (17, 16, 15), H_2 (2).

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- [1] G. A. Somorjai, *MRS Bull.* **1998**, 11–29.
- [2] X. W. Lou, H. C. Zeng, *J. Am. Chem. Soc.* **2003**, 125, 2697–2704.
- [3] X. W. Lou, H. C. Zeng, *Chem. Mater.* **2002**, 14, 4781–4789.
- [4] W. Y. Li, F. Y. Cheng, Z. L. Tao, J. Chen, *J. Phys. Chem. B* **2006**, 110, 119–124.
- [5] S. T. Wang, Y. G. Zhang, W. Z. Wang, G. L. Li, X. C. Ma, X. B. Li, Z. D. Zhang, Y. T. Qian, *J. Cryst. Growth* **2006**, 290, 96–102.
- [6] W. Chen, L. Q. Mai, Y. Y. Qi, Y. Dai, *J. Phys. Chem. Solids* **2006**, 67, 896–902.
- [7] P. Badica, *Cryst. Growth Des.* **2007**, 7, 794–801.
- [8] X. K. Hu, Y. T. Qian, Z. T. Song, J. R. Huang, R. Cao, J. Q. Xiao, *Chem. Mater.* **2008**, 20, 1527–1533.

- [9] G. T. Chandrappa, J. Livage, *Synth. Commun. Synth. React. Inorg. Met.-Org. Nano-Metal Chem.* **2006**, *36*, 23–28.
- [10] D. M. Antonelli, M. Trudeau, *Angew. Chem.* **1999**, *111*, 1555–1559; *Angew. Chem. Int. Ed.* **1999**, *38*, 1471–1475.
- [11] S. Suzuki, Y. Ohminami, T. Tsutsumi, M. M. Shoaib, M. Ichikawa, K. Asakura, *Chem. Lett.* **2003**, *32*, 1098–1099.
- [12] S. Sato, H. Niimi, S. Suzuki, W. J. Chun, K. Irokawa, H. Kuroda, K. Asakura, *Chem. Lett.* **2004**, *33*, 558–559.
- [13] M. Dieterle, G. Weinberg, G. Mestl, *Phys. Chem. Chem. Phys.* **2002**, *4*, 812–821.
- [14] R. Coquet, D. J. Willock, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3819–3828.
- [15] R. Tokarz-Sobieraj, K. Hermann, M. Witko, A. Blume, G. Mestl, R. Schlogl, *Surf. Sci.* **2001**, *489*, 107–125.
- [16] M. Chen, U. V. Waghmare, C. M. Friend, E. Kaxiras, *J. Chem. Phys.* **1998**, *109*, 6854–6860.
- [17] J. N. Allison, W. A. Goddard, *J. Catal.* **1985**, *92*, 127–135.
- [18] N. Ohler, A. T. Bell, *J. Phys. Chem. B* **2006**, *110*, 2700–2709.
- [19] F. Wang, W. Ueda, *Chem. Lett.* **2008**, *37*, 184–185.
- [20] P. Cheung, H. C. Liu, E. Iglesia, *J. Phys. Chem. B* **2004**, *108*, 18650–18658.
- [21] H. C. Liu, P. Cheung, E. Iglesia, *J. Phys. Chem. B* **2003**, *107*, 4118–4127.
- [22] A. Khodakov, J. Yang, S. Su, E. Iglesia, A. T. Bell, *J. Catal.* **1998**, *177*, 343–351.
- [23] K. D. Chen, A. T. Bell, E. Iglesia, *J. Phys. Chem. B* **2000**, *104*, 1292–1299.
- [24] M. D. Argyle, K. D. Chen, A. T. Bell, E. Iglesia, *J. Catal.* **2002**, *208*, 139–149.
- [25] J. Haber, E. Lalik, *Catal. Today* **1997**, *33*, 119–137.
- [26] M. B. J. Roeffaers, B. F. Sels, H. Uji-i, F. C. De Schryver, P. A. Jacobs, D. E. De Vos, J. Hofkens, *Nature* **2006**, *439*, 572–575.
- [27] W. E. Farneth, E. M. Mccarron, A. W. Sleight, R. H. Staley, *Langmuir* **1987**, *3*, 217–223.
- [28] W. E. Farneth, R. H. Staley, P. J. Domaille, R. D. Farlee, *J. Am. Chem. Soc.* **1987**, *109*, 4018–4023.
- [29] B. M. Choudary, K. V. S. Ranganath, U. Pal, M. L. Kantam, B. Sreedhar, *J. Am. Chem. Soc.* **2005**, *127*, 13167–13171.
- [30] B. M. Choudary, M. L. Kantam, K. V. S. Ranganath, K. Mahendar, B. Sreedhar, *J. Am. Chem. Soc.* **2004**, *126*, 3396–3397.
- [31] J. Zhu, J. A. Farmer, N. Ruzycy, L. Xu, C. T. Campbell, G. Henkelman, *J. Am. Chem. Soc.* **2008**, *130*, 2314–2322.
- [32] K. K. Zhu, J. C. Hu, C. Kubel, R. Richards, *Angew. Chem.* **2006**, *118*, 7435–7439; *Angew. Chem. Int. Ed.* **2006**, *45*, 7277–7281.
- [33] M. J. Climent, A. Corma, S. Iborra, M. Mifsud, *J. Catal.* **2007**, *247*, 223–230.
- [34] S. Carrettin, P. Concepcion, A. Corma, J. M. L. Nieto, V. F. Puentes, *Angew. Chem.* **2004**, *116*, 2592–2594; *Angew. Chem. Int. Ed.* **2004**, *43*, 2538–2540.
- [35] S. Yurdakal, G. Palmisano, V. Loddo, V. Augugliaro, L. Palmisano, *J. Am. Chem. Soc.* **2008**, *130*, 1568–1569.
- [36] M. A. Naik, B. G. Mishra, A. Dubey, *Colloids Surf. A* **2008**, *317*, 234–238.
- [37] F. Wang, W. Ueda, *Chem. Commun.* **2008**, 3196–3198.
- [38] G. A. Olah, *Friedel-Crafts Chemistry*, Wiley, New York, **1973**.
- [39] M. Noji, Y. Konno, K. Ishii, *J. Org. Chem.* **2007**, *72*, 5161–5167.
- [40] M. Rueping, B. J. Nachtsheim, W. Ieawsuwan, *Adv. Synth. Catal.* **2006**, *348*, 1033–1037.
- [41] K. Mertins, I. Iovel, J. Kischel, A. Zapf, M. Beller, *Angew. Chem.* **2005**, *117*, 242–246; *Angew. Chem. Int. Ed.* **2005**, *44*, 238–242.
- [42] K. Motokura, N. Nakagiri, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Org. Chem.* **2007**, *72*, 6006–6015.
- [43] B. M. Devassy, G. V. Shanbhag, F. Lefebvre, W. Bohringer, J. Fletcher, S. B. Halligudi, *J. Mol. Catal. A* **2005**, *230*, 113–119.
- [44] Y. X. Rao, M. Trudeau, D. Antonelli, *J. Am. Chem. Soc.* **2006**, *128*, 13996–13997.
- [45] B. M. Choudary, R. S. Mulukutla, K. J. Klabunde, *J. Am. Chem. Soc.* **2003**, *125*, 2020–2021.
- [46] K. Yamashita, M. Hirano, K. Okumura, M. Niwa, *Catal. Today* **2006**, *118*, 385–391.
- [47] T. Yamato, C. Hideshima, G. K. S. Prakash, G. A. Olah, *J. Org. Chem.* **1991**, *56*, 2089–2091.
- [48] M. Iwamoto, H. Furukawa, K. Matsukami, T. Takenaka, S. Kagawa, *J. Am. Chem. Soc.* **1983**, *105*, 3719–3720.
- [49] S. K. Jana, *Catal. Surv. Jpn.* **2005**, *9*, 25–34.
- [50] M. J. Jones, *Organic Chemistry*, W. W. Norton & Company, **1997**, pp. 203–204.
- [51] P. Beltrame, G. Zuretti, *Appl. Catal. A* **2005**, *283*, 33–38.
- [52] S. Himeno, H. Niiya, T. Ueda, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 631–637.
- [53] A. Muller, S. Roy, in *The Chemistry of Nanomaterials Synthesis, Properties and Applications*, Vol. 2 (Eds.: C. N. R. Rao, A. Muller, A. K. Cheetham), Wiley-VCH, Weinheim, **2004**, pp. 452–475.
- [54] G. Mestl, N. F. D. Verbruggen, H. Knozinger, *Langmuir* **1995**, *11*, 3035–3041.
- [55] R. Burch, *J. Chem. Soc. Faraday Trans. 1* **1978**, *74*, 2982–2990.
- [56] N. Katada, H. Igi, J. H. Kim, M. Niwa, *J. Phys. Chem. B* **1997**, *101*, 5969–5977.
- [57] J. L. Falconer, J. A. Schwarz, *Catal. Rev. Sci. Eng.* **1983**, *25*, 141–227.
- [58] K. Dyrek, M. Che, *Chem. Rev.* **1997**, *97*, 305–331.
- [59] M. Anwar, C. A. Hogarth, K. A. K. Lott, *J. Mater. Sci.* **1989**, *24*, 1660–1664.
- [60] M. Chiesa, M. C. Paganini, E. Giamello, D. M. Murphy, C. Di Valentin, G. Pacchioni, *Acc. Chem. Res.* **2006**, *39*, 861–867.
- [61] A. Moissette, H. Vezin, I. Gener, J. Patarin, C. Bremard, *Angew. Chem.* **2002**, *114*, 1289; *Angew. Chem. Int. Ed.* **2002**, *41*, 1241–+.
- [62] S. Matsushita, Y. Toda, M. Miyakawa, K. Hayashi, T. Kamiya, M. Hirano, I. Tanaka, H. Hosono, *Science* **2003**, *301*, 626–629.
- [63] D. V. Mesaros, C. Dybowski, *Langmuir* **1988**, *4*, 983–988.
- [64] J. F. Moulder, F. S. William, E. S. Peter, D. B. Kenneth, *Handbook of X Ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of Xps Data*, Physical Electronics, **1995**.
- [65] K. D. Chen, A. T. Bell, E. Iglesia, *J. Catal.* **2002**, *209*, 35–42.
- [66] R. S. Weber, *J. Catal.* **1995**, *151*, 470–474.
- [67] N. Ichikuni, H. Murayama, S. Shimazu, T. Uematsu, *Catal. Lett.* **2004**, *93*, 177–180.
- [68] M. Che, C. Naccache, B. Imelik, *J. Catal.* **1972**, *24*, 328–335.
- [69] Y. Oaki, H. Imai, *Angew. Chem.* **2007**, *119*, 5039–5043; *Angew. Chem. Int. Ed.* **2007**, *46*, 4951–4955.
- [70] Y. Omomo, T. Sasaki, L. Z. Wang, M. Watanabe, *J. Am. Chem. Soc.* **2003**, *125*, 3568–3575.
- [71] S. Sugunan, G. D. Rani, K. B. Sherly, *React. Kinet. Catal. Lett.* **1991**, *43*, 375–380.
- [72] H. F. Askal, *Talanta* **1997**, *44*, 1749–1755.
- [73] A. M. El-Brashy, M. E. S. Metwally, F. A. El-Sepai, *Bull. Korean Chem. Soc.* **2004**, *25*, 365–372.
- [74] G. Mestl, T. K. K. Srinivasan, H. Knoezinger, *Langmuir* **1995**, *11*, 3795–3804.
- [75] M. Kurumada, C. Kaito, *J. Phys. Soc. Jpn.* **2006**, *75*, -.
- [76] P. K. Sharma, M. H. Jilavi, R. Nass, H. Schmidt, *J. Lumin.* **1999**, *82*, 187–193.
- [77] D. Gallagher, W. E. Heady, J. M. Racz, R. N. Bhargava, *J. Cryst. Growth* **1994**, *138*, 970–975.
- [78] G. Busca, *Langmuir* **1986**, *2*, 577–582.
- [79] L. Fang, Y. Y. Shu, A. Q. Wang, T. Zhang, *J. Phys. Chem. C* **2007**, *111*, 2401–2408.
- [80] T. Mizushima, K. Fukushima, H. Ohkita, N. Kakuta, *Appl. Catal. A* **2007**, *326*, 106–112.
- [81] S. Brunauer, P. H. Emmett, E. Teller, *J. Am. Chem. Soc.* **1938**, *60*, 309–319.

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